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HYDROCARBON POLYMERIC BINDER

FOR ADVANCED SOLID PROPELLANT

SECOND ADDENDUM TO TRIENNIAL REPORT

PERIOD COVERED: October 1, 1969

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Report Edited By: James E. Potts

Contributors: A. C. Ashcraft, Jr.
J. E. Potts UCC
E. W. Wise

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Technically Managed By: H. E. Marsh, Jr. - JPL

UNION CARBIDE CORPORATION
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Polymer Research and Development
Bound Brook, New Jersey

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TECHNICAL CONTENT STATEMENT

This report contains information prepared by Union Carbide Corporation, Chemicals and Plastics Operations Division, under J. P. L. subcontract. Its content is not necessarily endorsed by the Jet Propulsion Laboratory, California Institute of Technology or the National Aeronautics and Space Administration.

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I. OBJECTIVE

Union Carbide Corporation, Chemicals and Plastics Operations Division has agreed to assist the Jet Propulsion Laboratory, California Institute of Technology, on a level of effort basis, in the development of a new or improved polymeric binder for advanced solid propellants.

The general objectives are described in Quarterly Report No. 1.

II. SUMMARY

Part 1

Terpolymers of ethylene, propylene and vinyl acetate were converted to the corresponding vinyl alcohol terpolymers by hydrogenolysis (See first addendum to triennial report part 2-C). These terpolymers cured readily even at an average functionality of 1.24 when reacted with an equivalent amount of diisocyanate. Shore-A hardness, tensile modulus and tensile strength of cured gumstocks were found to increase with increasing average functionality, however, the elongation at break decreased with increasing functionality, and remained below 60% over the whole range of functionalities examined.

Terpolymerization of ethylene, propylene and vinyl acetate with diethylazobisisobutyrate initiator was used to prepare terpolymers containing one terminal ester group per molecule and an additional average functionality of one vinyl acetate residue per molecule. These terpolymers were reduced (both catalytically, using copper chromite catalyst and hydrogen, and chemically, using lithium aluminum hydride) to give curable prepolymers with hydroxyl functionality, part terminal and part randomly placed. The properties of diisocyanate cured test bars prepared with these prepolymers were intermediate in properties between the random functionality terpolymers and prepolymers having exclusively terminal functionality.

Part 2

A saturated polyisoprene derivative is described having terminal methyl ester functionality. From this material, carboxy-telechelic as well as hydroxy-telechelic diol prepolymers were prepared using melt saponification and LiAlH_4 reduction respectively.

A larger sample of ester terminated polymer was polymerized and subsequently converted to the hydroxy-telechelic product using catalytic hydrogenolysis.

Polyurethane curing studies were done on the above which resulted in soft highly extensible elastomeric gumstocks.

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Hydroxy-telechelic polymer 29-EMS-72 prepared by copper chromite hydrogenolysis of ester-telechelic polyisoprene 29-EMS-70" was cured in polyurethane formulations using toluene diisocyanate and trimethylol propane. The gumstock prepared at the 5% triol level had an elongation at break of over 1000% and showed very good adhesion to the steel end tabs on the tensile test specimens. Lithium aluminum hydride reduction of 29-EMS-70 provided another diol polymer 9170-143-1 for comparison with 29-EMS-72.

Both of these polymers were analyzed by thin layer chromatography from which it was concluded that no components other than the difunctional component was likely to be present in either 29-EMS-72 or 9170-143-1.

Polymerization run 30-EMS-18 afforded an additional 3.35 kg of the ester-telechelic product which has been reduced to afford a larger sample of hydroxy-telechelic polymer for J. P. L. evaluation.

The technique of Gel Permeation Chromatography has been used to determine the molecular weight distribution of 29-EMS-72, a sample of hydroxy-telechelic liquid saturated hydrocarbon prepolymer. This prepolymer was prepared by hydrogenolysis of an ester-telechelic polyisoprene. 29-EMS-72 had an $\bar{M}_w/\bar{M}_n$ ratio of 1.73.

Part 3

Two samples of hydroxy-telechelic polyisoprene, 9170-117-2 and 9528-54-6 were prepared by the method of DEAB initiated free radical polymerization followed by LiAlH_4 reduction of the endgroups. This method was chosen to avoid saturation of the polymer chain. The resultant unsaturated diols were submitted to J. P. L. for evaluation.

Diethyl azobisisobutyrate was used to prepare two ester-telechelic liquid polyisoprenes using the continuous stirred autoclave reactor. These products were subsequently reduced with lithium aluminum hydride to give two samples of hydroxy-telechelic liquid polyisoprene, one having a molecular weight of 2225, the other 2454.

Gel Permeation Chromatography (G. P. C.) was used to determine the molecular weight distributions in hydroxy-telechelic polyisoprene samples A, B, C and D. The molecular weight distributions were monomodal and narrow with the polydispersity index, $\bar{A}_w/\bar{A}_n$, increasing with molecular weight from 1.5 at a $\bar{M}_n$ of 1200 up to about 2.0 at a molecular weight of 2900. A very good correlation was obtained between the values of $\bar{A}_n$ determined by GPC and $\bar{M}_n$ values determined by vapor pressure osmometry.

Various experimental factors were examined to determine the source of difficulty in an isoprene polymerization in the 5-gallon reactor which gave a non-uniform product of low functionality. It was concluded that process improvements relating to initiator and monomer purity were desirable, but that the main difficulty was in the initiator feed system. A new pumping system was installed and an analog simulation of the reactor, feed system and initiator decomposition kinetics was devised which permits the selection of initial initiator concentrations and feed rates to use to give a nearly uniform initiator concentration throughout a polymerization run. An isoprene polymerization was run in which the process improvements were implemented. This run resulted in the preparation of an ester telechelic polyisoprene of $2290 \bar{M}_n$ having an average functionality of $1.98 \pm .02$.

III. SCOPE

The scope of our program remains as previously outlined.

IV. INTRODUCTION

During the period covered in our last addendum to the triennial report our experimental program had been directed towards the preparation, characterization and evaluation of ethylene/propylene terpolymers in which the reactive functionality was supplied by the third monomer. For example, a predominantly ethylene/propylene copolymer with randomly placed tertiary hydroxyl functionality was prepared from the terpolymerization of ethylene, propylene and 3-hydroxy-3-methylbutene-1, the latter being added in sufficient concentration to permit the incorporation of about two hydroxyl groups, on the average, per molecule. We also discussed the preparation of ethylene/propylene/vinyl acetate terpolymers and their hydrolysis to give liquid prepolymers with randomly placed hydroxyl functionality.

In this report the results of curing studies on these products are presented, as well as the results of some terpolymerizations in which part of the functionality is introduced in terminal positions by means of the free radical initiator employed.

Although these random functionality terpolymers cured readily using diisocyanates to give soft rubbery gumstocks, the resulting mechanical properties were deficient, notably the maximum elongation at break. The latter property was found to be dependant upon average functionality, but was never greater than 60%. Products with average functionalities in excess of two gave highly crosslinked somewhat harder gumstocks but having elongation at break as low as 20%.

A significant improvement in properties resulted from the introduction of some terminal functionality. For example, a terpolymer of ethylene, propylene and vinyl acetate was prepared using the azo initiator diethyl azobisisobutyrate (DEAB). This product had one terminal ester per molecule and on the average, one additional ester group derived from vinyl acetate placed randomly along the chain. Hydride reduction of these ester groups gave a hydroxyl functionality prepolymer, curable with diisocyanates. The resulting gumstock had an elongation at break of 75%, better than any terpolymer having strictly random functionality, but inferior to that obtainable with a truly telechelic product.

In view of these results, we have concentrated our current synthetic program on the preparation of saturated telechelic liquid prepolymers containing no randomly placed functional groups.

The report to follow will discuss the preparation of ester telechelic liquid hydrocarbon polymers and their conversion by hydrolysis or reduction to give prepolymers with carboxyl or hydroxyl functionality.

V. TECHNICAL DISCUSSION, PART 1 -

PREPOLYMERS CONTAINING RANDOMLY PLACED FUNCTIONAL GROUPS

A. Curing Studies on Ethylene/Propylene/Vinyl Alcohol
Prepolymers:

The preparation of ethylene/propylene/vinyl alcohol prepolymers having a range of average alcohol functionality was discussed in part V-A-2 of our quarterly report for July-October of 1969. Four different prepolymers were obtained in which the hydroxyl functionality varied from 1.24 up to 2.67.

The formulations listed in Table I were prepared and test bars cast using the mold described in Figure 6 of our first annual addendum to our triennial report. The resulting test bars are 3/8" by 3/8" by 2" and have adhering steel end tabs for clamping in an Instron tester. After the formulations had been cured at the indicated temperature for the indicated time, the test bars were removed and used to determine uniaxial stress/strain characteristics on an Instron tester. Shore-A hardness determinations were then made on the broken bars. The results of the measurements are summarized in Figure 1. Note that the hardness, tensile strength and modulus increase with increasing functionality, whereas the elongation at break decreases with increasing functionality over the entire functionality range examined.

The fact that all of the formulations cured, including the one containing 1.24 functionality prepolymer is believed to indicate that a very broad functionality distribution exists in these random terpolymers with substantial quantities of higher functionality material present even in the lowest average functionality prepolymer.

ISOCYANATE CURING OF HYDROLYZED ETHYLENE/PROPYLENE/VINYL ACETATE TERPOLYMERS

TABLE I

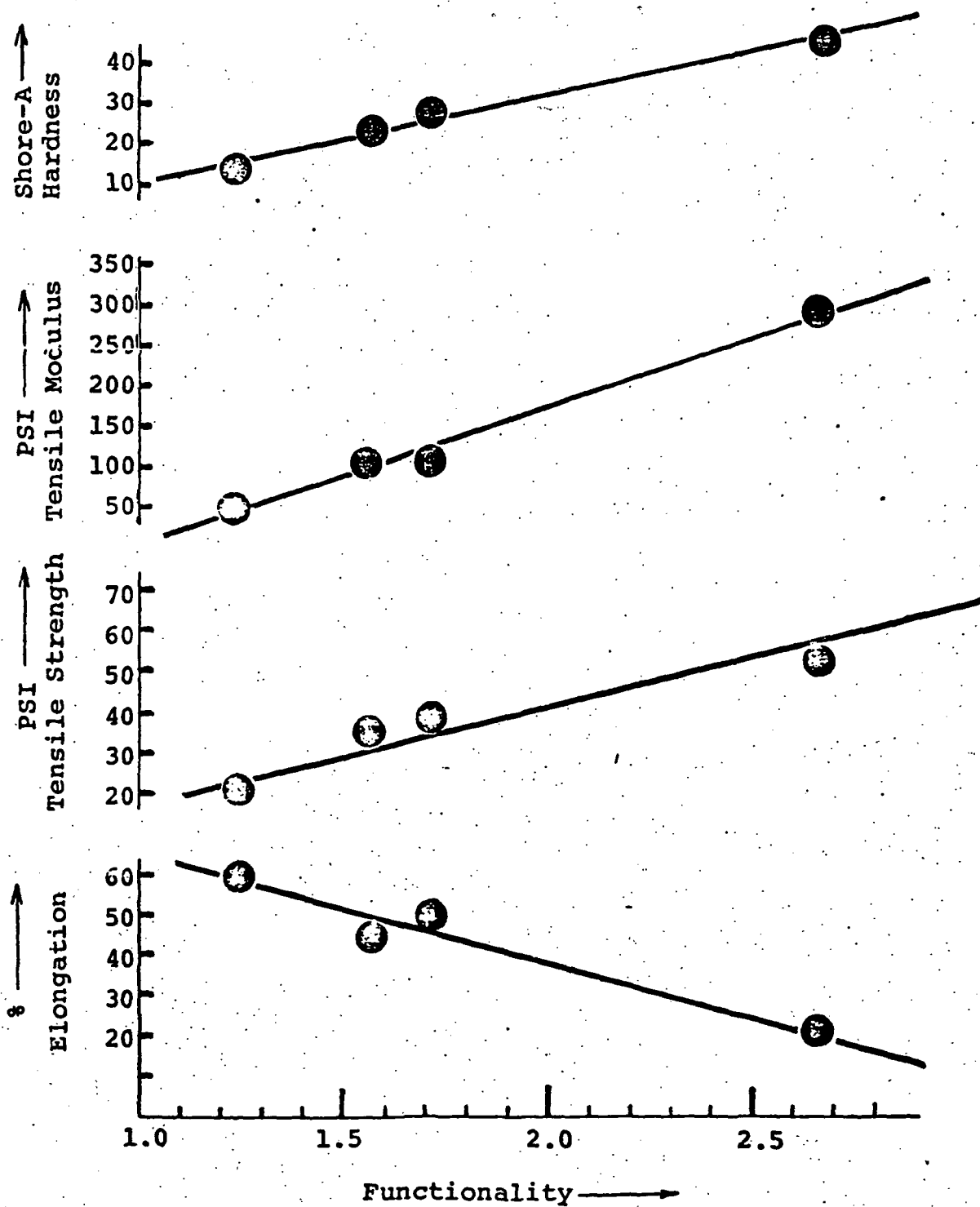
<u>Formulation</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
Notebook Reference, 9170-	67	80	86	86
Prepolymer used, 9170-	65	73	78	84
Prepolymer Functionality	2.67	1.56	1.72	1.24
Grams Prepolymer	32.983	5.00	10.766	11.725
Milliequivalents OH	33.26	4.64	9.83	9.79
Isocyanate Used	HDIA	TDIb	TDIb	TDIb
Grams Isocyanate	2.641	.403	0.857	0.852
Milliequivalents NCO	31.38	4.64	9.84	9.78
NCO/OH Ratio	0.94	1.00	1.00	1.00
Cure Temperature	23°C	60°C	60°C	60°C
Cure Time	60 days	18 hrs	18 hrs	18 hrs
<u>Cured Gumstock Properties</u>				
Shore-A Hardness	45	23	26	14
Tensile Modulus, psi	288	111	104	52
Tensile Strength, psi	52	36	38	23
% Elongation at Break	22	45	50	60

a. HDI, hexamethylenediisocyanate

b. TDI, toluene diisocyanate

FIGURE 1

VARIATION OF CURED GUMSTOCK PROPERTIES
WITH PREPOLYMER FUNCTIONALITY

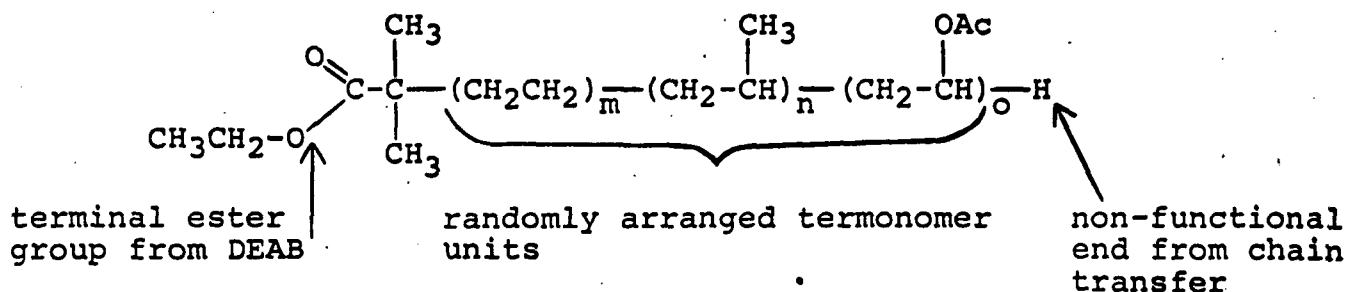


B. Preparation of Terpolymers Containing Partially Terminal Functionality

The prepolymers containing randomly placed functionality were found to give crosslinked dimensionally stable soft rubber cures using only diisocyanates. This was the case even when the average functionality was as low as 1.24. The reason for this behavior is probably related to the random placement of the functional groups along the polymer chain and the fact that a range of molecular sizes is present in a given terpolymer sample due to the finite molecular weight distribution.

These factors make it possible for a terpolymer with an average functionality of 1.5 to contain sufficient higher functionality molecules (3 or greater) for the formation of a gelled structure when reacted with a difunctional isocyanate. However, regardless of their curing characteristics, the terpolymer based prepolymers so far examined have not given sufficiently extensible rubbers upon curing to permit high solids loadings.

In an attempt to obtain ethylene/propylene based prepolymers giving more extensible rubbers, we modified our terpolymer synthesis so as to introduce some terminal functionality. Instead of AIBN or DTBP initiators, we used DEAB, diethyl azobisisobutyrate*, and included enough vinyl acetate in the charge to provide approximately one acetate unit per molecule on the average. This provided a terpolymer which had the following structure:



The polymerization conditions used and analytical data on the resulting terpolymers are summarized in Table II.

High pressure hydrogenation over a copper chromite catalyst was then utilized to convert the terminal ester groups as well as the vinyl acetate residues to hydroxyl functional groups, part of which are terminal (one on each molecule) and the remainder randomly arranged.

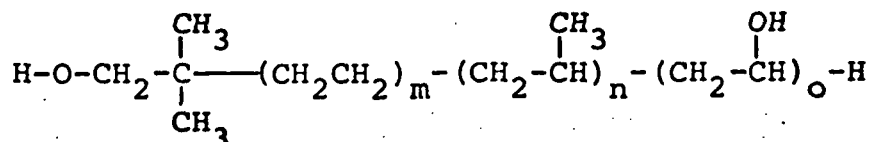
* In our previous work with DEAB, we found that monomers such as ethylene gave monofunctional ester terminated polymers when DEAB was used as the initiator.

TABLE II

PREPARATION OF ETHYLENE/PROPYLENE/VINYL ACETATE TERPOLYMERS
WITH TERMINAL ESTER FUNCTIONALITY

<u>Run No.</u>	<u>28-EMS-130</u>	<u>29-EMS-3</u>
<u>Charge Composition, Wt. %</u>		
Ethylene	47.53	47.64
Propylene	47.53	47.64
Vinyl Acetate	3.96	3.74
DEAB	0.98	0.98
<u>Reaction Conditions</u>		
Temperature, °C	127-137	130-139
Pressure, mpsi	25	25
Hold-Up Time, min.	10.20	7.35
Feed Rate, gms/hr	5419	7497
<u>Productivity</u>		
Yield, gms	1827	1965
Conversion, %	19.23	16.67
Production Rate, gms/hr	1032	1236
<u>Physical & Chemical Properties</u>		
Molecular Weight	2040	2274
Brookfield Viscosity, poise	113	143
Reduced Viscosity	.122	.100
Vitrification Temperature	-55°C	-58°C
Saponification Equivalent	827	1087
Ester Functionality	2.47	2.09

The reduction was accomplished in an overnight hydrogenation (17-3/4 hrs) at 260°C and 4875 psi hydrogen pressure. The product, designated 28-EMS-135, had a molecular weight of 2019 and a hydroxyl equivalent weight of 1191 indicating an average functionality of 1.70. The discrepancy between this value and the precursor's ester functionality of 2.47 most likely is due to partial acetate pyrolysis followed by double bond hydrogenation. The structure expected for this product is:



This product was expected to lead to cured gum-stocks having mechanical properties superior to those of the prepolymers containing exclusively randomly arranged functionality. To test this hypothesis, the formulation outlined below was prepared and cured at 75°C for 41 hours in the previously described mold:

Gms. 28-EMS-135	7.109
Milliequivalents OH	5.97
Gms. Hexamethylene Diisocyanate	0.536
Milliequivalents NCO	6.86
NCO/OH Ratio	1.15

The resultant test bar was a clear colorless soft rubber having a Shore-A hardness of 23%, a tensile modulus of 104 psi, a tensile strength of 33 psi and a 75% elongation at break with complete recovery after break. The elongation obtained is a considerable improvement over the best values we have obtained with the terpolymers containing only randomly located functionality.

Lithium aluminum hydride was also used to reduce terpolymer 28-EMS-130. 100 Grams of the terpolymer was treated with 12 grams LiAlH₄ in anhydrous ethyl ether. 96 Grams of fully reduced product 24-JCW-32-C was recovered. The product had a molecular weight of 1862 and an OH equivalent weight of 991 indicating an average functionality of 1.88 OH per molecule. The molecular weight obtained is suspect since the starting material had an $\bar{M}_n$ of 2040, and the fractionation sometimes encountered in a workup of a reaction mixture generally raises the molecular weight. A value of 2019 (as was obtained in 28-EMS-135 from the same precursor) would lead to a functionality of 2.04.

We anticipate that a prepolymer such as 28-EMS-135 or 24-JCW-32-C would make a very useful contribution to urethane binder formulations replacing the low molecular weight triols (such as trimethylol propane) currently used to provide crosslinking of diisocyanate cures on telechelic diol prepolymers. The advantages of such a crosslinker would result from improved compatibility with hydrocarbon prepolymers and a more open gel structure having less crowding of polymer chains near crosslink sites.

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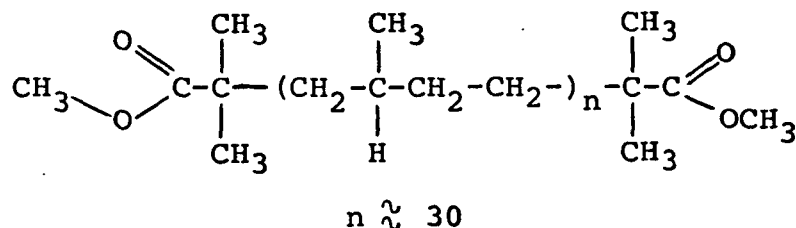
V. TECHNICAL DISCUSSION, PART 2 -

SATURATED HYDROCARBON PREPOLYMERS CONTAINING

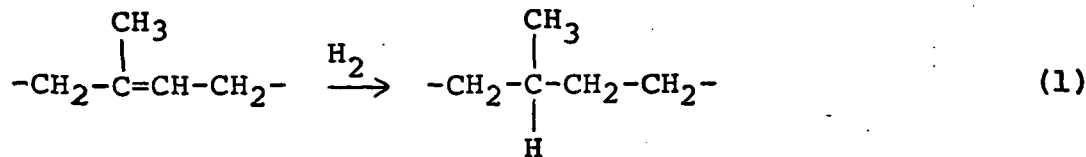
EXCLUSIVELY TERMINAL FUNCTIONAL GROUPS

A. Preparation of Carboxy and Hydroxy Telechelic Saturated Liquid Hydrocarbon Polymers

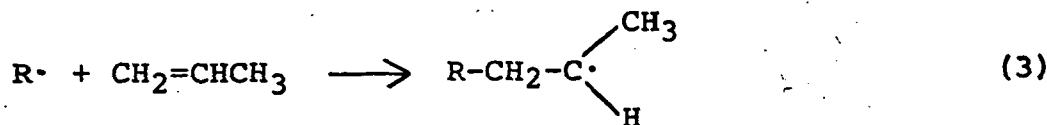
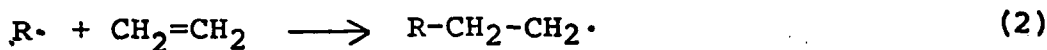
We have prepared a telechelic ester terminated saturated liquid polymer, the structure of which is shown below:



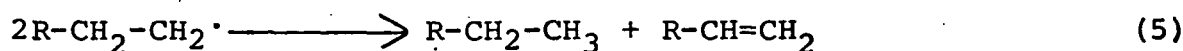
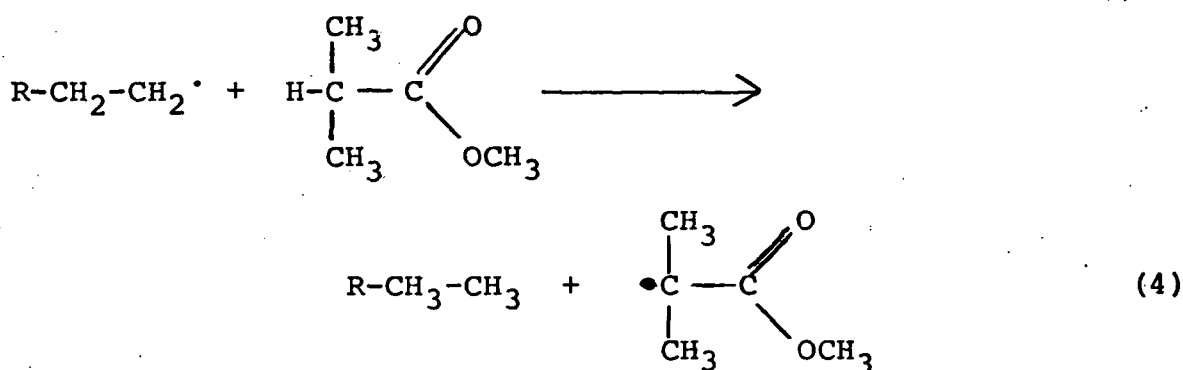
The ester end groups are derived from dimethyl azobis-isobutyrate (DMAB) initiator, and the saturated hydrocarbon backbone is derived from a linear 1-4 polyisoprene chain which was subsequently hydrogenated over Raney Nickel catalyst. This procedure results in the conversion of the 1-4 isoprene residues into sequences of alternating ethylene/propylene residues:



The advantage of this route to an ethylene/propylene copolymer over the direct copolymerization route stems from the nature of the propagating polymer chain radical involved. In the case of the ethylene copolymerization route, the polymeric radicals are unstabilized, and therefore extremely reactive, alkyl radicals:

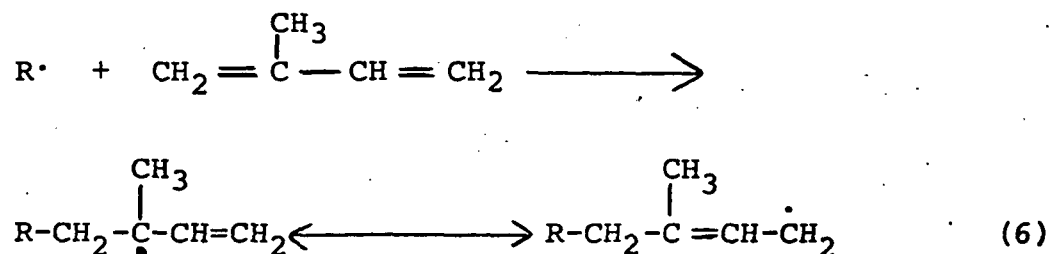


These reactive species can abstract hydrogen atoms from many different sources, such as the α -position of an ester, or even another radical:

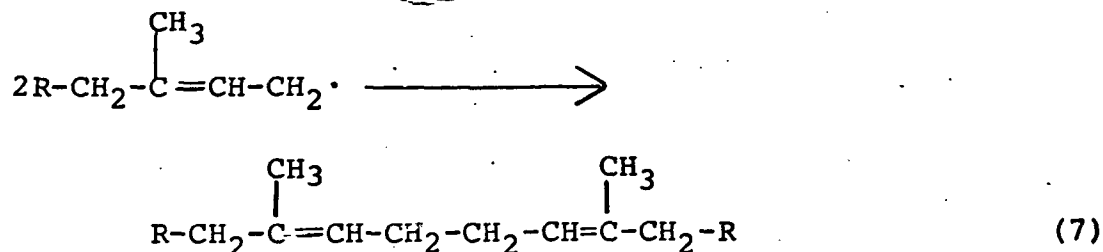


Reaction (4) is an example of chain transfer and reaction (5) is termination by disproportionation. Both of these processes lead to "non-functional" chain ends, that is, ends not derived from an initiator radical, and therefore not containing the desired functional group.

On the other hand, the radicals encountered in the polymerization of isoprene are stabilized by resonance between two alternate allylic radical forms and are relatively unreactive toward hydrogen abstraction reactions:



Only the most active hydrogen donors, such as mercaptans can serve as chain transfer agents in diene polymerizations, and the dominant mode of chain termination is by coupling:



This produces difunctional molecules only, with the result that the "copolymer" produced by hydrogenating the polyisoprene is also difunctional.

The first run, 28-EMS-64 was polymerized in the small batch stirred autoclave reactor (polymerization run #28-EMS-48) according to the procedure outlined in table III, and subsequently hydrogenated at 4000 psi hydrogen pressure and 125°C over active Raney Nickel catalyst. This produced 61 grams of saturated ester telechelic polymer.

Nuclear magnetic resonance spectroscopy permitted an end group analysis which gave an ester equivalent weight of 1055 for this material. Vapor Pressure Osmometry was used to measure the number average molecular weight which was found to be 2225. These results imply an ester functionality of 2.1.

This ester terminated product can be considered as the precursor to either carboxy telechelic or hydroxy telechelic polymers, the former being derived by hydrolysis, the latter by reduction. To verify this, 10.3 grams (9 meq. ester) of 28-EMS-64 was saponified in the melt at 170°C by the addition of 30 mg. KOH as a 5.89 N solution. After the small quantity of water had flashed off the saponification proceeded rapidly with large increase in melt viscosity as the concentration of potassium carboxylate groups increased. Fifteen minutes after the addition of the KOH the formerly quite fluid melt had assumed a thick taffy-like consistency and could no longer be stirred.* Acidification with acetic acid gave the liquid, heptane soluble carboxyl terminated prepolymer (designated 9170-88-5) in 7.8 grams yield.

* The great increase in viscosity near the end of the melt saponification of this telechelic polymer was not unexpected and is believed to be the result of chain extension through partial ionic bonds at the chain ends analogous to the reversible crosslinks in ionomer type high polymers.

TABLE III

ISOPRENE POLYMERIZATION RUN 28-EMS-48

Charged To Reactor

Isoprene	530g
Benzene	88g
DMAB	1.72g

Fed In During Reaction

Benzene	242g
DMAB	15.5g

Reaction Conditions

Temperature	89-94°C
Pressure	
Initial	40 psi
Final	80 psi
Time	3.25 hrs.

Productivity

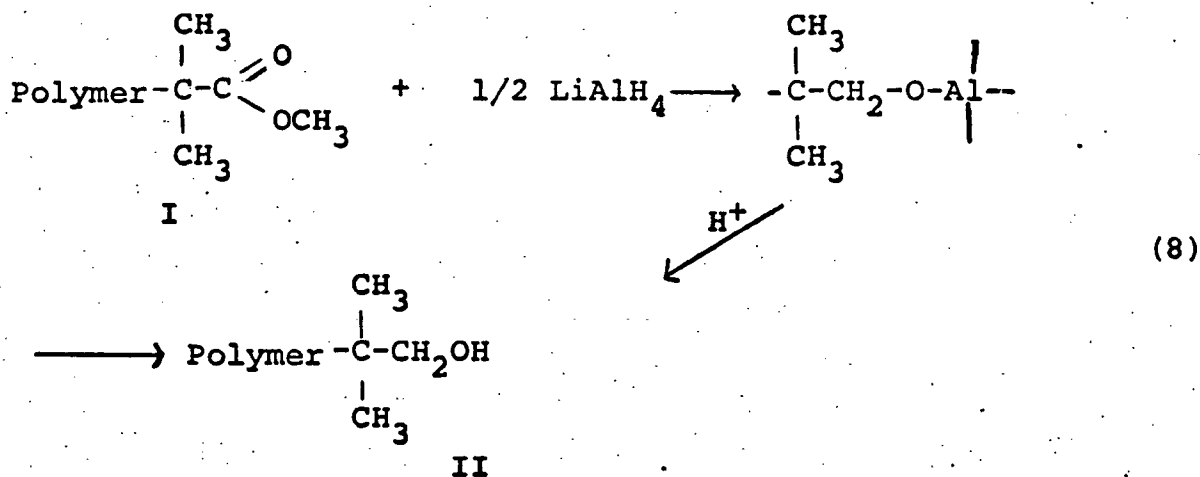
Yield	154 gms
Conversion	29%
Rate	8.94%/hr.

Thin layer chromatography on silica gel plates using 1% methanol in chloroform as the developing solvent, disclosed a single uniform spindle shaped streak - just what one would expect to result from a single functionality type with a superimposed distribution of molecular weights.

To determine the number average molecular weight of this carboxyl terminated polymer we used vapor pressure osmometry in tetrahydrofuran at 37°C. The measurements were then extrapolated to zero concentration. In this method association effects which can give erroneously high molecular weights for carboxyl containing polymers are eliminated as a source of error. The graphical extrapolation is shown in Figure 2.1. From the value of the intercept and a machine calibration factor K (determined using sucrose octa-acetate as a primary standard) we calculate a molecular weight of 2434.

Potentiometric titration using tetrabutylammonium hydroxide gave a neutralization equivalent of 1253. These measurements imply a carboxyl functionality of 1.94, a result consistent with the thin layer chromatographic analysis.

Having demonstrated that a carboxyl telechelic product could be prepared from the diester precursor we next attempted to reduce the ester end groups using lithium aluminum hydride. The proposed reaction is shown below:



1) In this case the fitted line was actually determined by a least squares fit of the original R vs C data to the equation:

$$R = A_1 C + A_2 C^2,$$

the parameter A_1 being identical with $(\Delta R/C)_{C=0}$ in Figure 2. The least squares fit to the quadratic passing through the origin, while mathematically equivalent to the graphical procedure, is preferable because it gives more realistic weighting to the measurements made at low concentration.

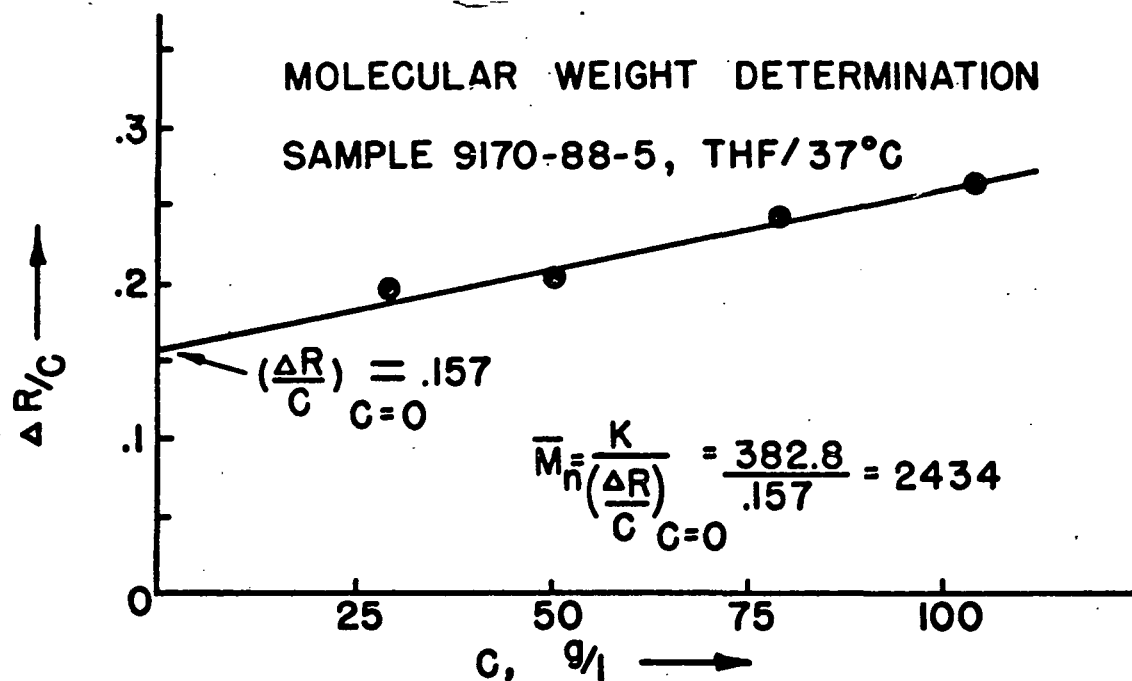


FIGURE 2.

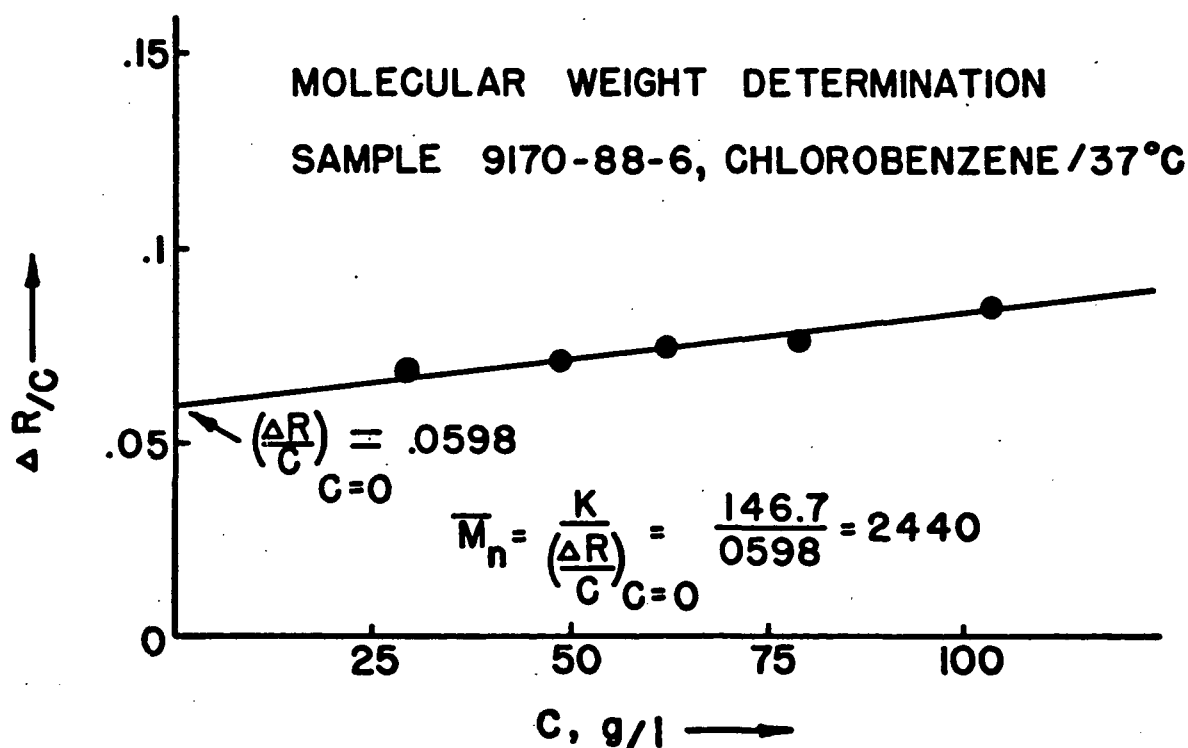


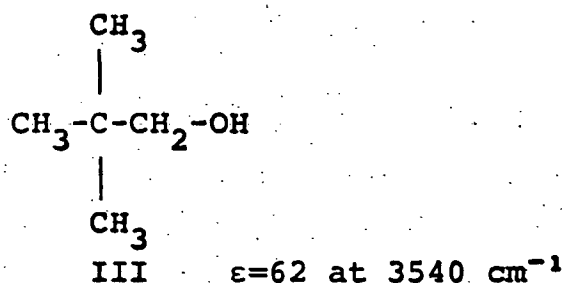
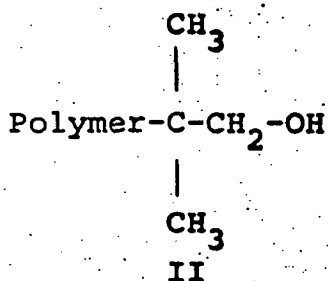
FIGURE 3.

This results in the formation of hindered primary hydroxyl groups on the chain ends. This type of hydroxyl functionality may offer unique advantages in polyurethane solid propellant binders: 1) primary urethane linkages are more thermally stable than either secondary or tertiary, and 2) the steric hindrance imposed by the geminal methyl groups should reduce the reactivity of the primary hydroxyl group and allow longer pot life in a propellant formulation than that attainable with a less hindered end group.

To accomplish the above reduction, 20 grams of 28-EMS-64 was treated with 6.34 grams lithium aluminum hydride in 50 ml absolute ether. After the reaction mixture had been heated under reflux for one hour, it was hydrolyzed to decompose the excess hydride by cautious addition of saturated aqueous ammonium chloride solution. The product was recovered by extraction with heptane, drying and evaporation to give 18.7 grams of liquid polymer, designated 9170-88-6.

Again, thin layer chromatography showed a single constituent (1:1 heptane/ CHCl_3 on Silica Gel) as a single spindle shaped streak on the plate from $R_f=0.0$ to 0.4. The molecular weight was measured by vapor pressure osmometry in chlorobenzene at 37°C . It was found to be 2440 (see Figure 3).

Using neopentyl alcohol (III below) as the model for the terminal hydroxyl groups in the reduced polymer (II below), the extinction coefficient of the hydroxyl absorption of III at 3540 cm^{-1} was determined using a Perkin Elmer model 21 infrared spectrophotometer. The solvent used to prepare the solutions was a 25 vol. % mixture of ethyl acetate in carbon tetrachloride, chosen to minimize problems due to hydrogen bonding. Having determined ϵ , the hydroxyl



terminated polymer could then be analyzed infrared spectroscopy to determine the hydroxyl equivalent weight. This was found to be 1254. The functionality is thus $2440/1254$ or 1.95 hydroxyl groups per molecule, a result consistent with the chromatographic study and with the functionalities of the related products 28-EMS-64 and 9170-88-5.

The difunctional hydroxyl terminated product 9170-88-6 was reacted with hexamethylene diisocyanate with trimethylol propane added to provide the necessary sites for crosslinking. The results of this study are summarized in Table IV.

The mechanical properties measured on the 2nd formulation represent lower limits only. After break had occurred, a large bubble was found near one of the steel end tabs at the location of the breaking point of the tensile specimen. Subsequent curing studies will be done using vacuum mixing in an attempt to avoid air bubbles. After breaking, both tensile bars contracted slowly until nearly the original dimensions were reached.

Another cure formulation was prepared in which a random hydroxyl functionality terpolymer was added to provide the branch points for the gel structure rather than trimethylol propane. This terpolymer, 9170-65-1, had $M_n=2646$, $F=2.67$ OH/molecule and was prepared by saponification of an ethylene/propylene/vinyl acetate terpolymer. The results are summarized in Table V.

Complete elastic recovery was noted after the break occurred. It is anticipated that lower polyol content would lead to a softer more extensible rubber by lowering the crosslink density. Due to the similarity of polymer backbone and molecular weight, the diol prepolymer and the polyol were highly compatible. This avoids the solubility problems encountered when crystalline polar triols, like trimethylol propane, are used to provide crosslinks in binder formulations.

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TABLE IV

POLYURETHANE CURE FORMULATIONS USING 9170-88-6

Formulation 9170-95-	1	2
Prepolymer, gms	4.9856	7.0153
Trimethylol Propane, gms	0.1429	0.2813
Hexamethylene Diisocyanate, gms	0.3406	0.5575
OH from diol, meq.	3.976	5.59
OH from triol, meq.	0.320	0.63
NCO form HDI, meq.	4.364	7.14
ρ =meq triol/meq. OH	.0705	.101
R=meq NCO/meq. OH	1.016	1.148
Cure Temperature	25°C	25°C
Cure Time, hrs.	48	48
Shore A Hardness	13	-
Initial Modulus, psi	95	63
Yield Strength, psi	17	7
Yield Elongation, %	125	50
Ultimate Tensile Strength, psi	14	4
Elongation at Break, %	1300	280

TABLE V

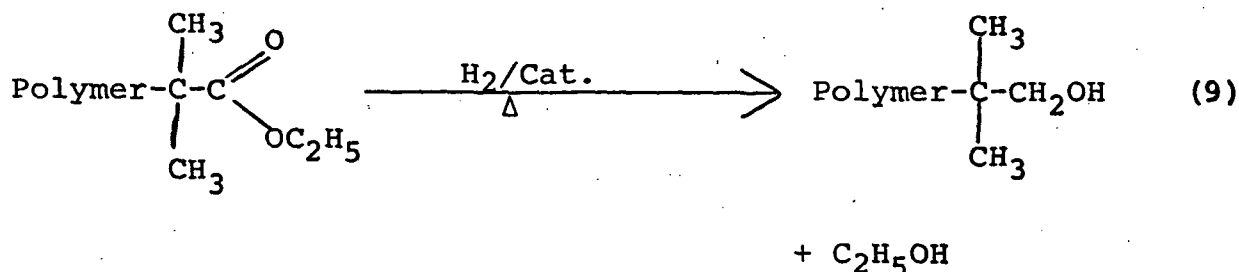
POLYURETHANE CURE FORMULATION USING 9170-88-6 AND
A RANDOM FUNCTIONALITY POLYOL

Formulation 9170-100-2	
Diol Prepolymer, gms	6.892
Polyol Prepolymer, gms	0.766
H.D.I. gms	0.601
OH from diol, meq.	5.51
OH from polyol, meq.	.77
NCO from HDI, meq.	7.14
R=meq. NCO/meq. OH	1.15
Cure Temperature	90°C
Cure Time	15 hrs.
Initial Modulus, psi	155
Yield Strength, psi	44
Yield Elongation, %	55
Ultimate Tensile Strength, psi	79
Elongation at Break	210

B. Preparation of a Larger Sample of the Hydroxy Telechelic Saturated Liquid Hydrocarbon Polymer

A larger sample of ester terminated telechelic polyisoprene was prepared in the continuous stirred autoclave reactor. Diethylazobisisobutyrate was used as the initiator in this run which yielded 476 grams of product, #29-EMS-70. The procedural details for this run are summarized in Table VI. The terminal ester groups were subsequently reduced by hydrogenolysis over copper chromite catalyst. This treatment also results in the hydrogenation of the double bonds in the polymer and gives a completely saturated liquid product. The conditions for the reduction are as follows: Using a hydrogen pressure ranging from 3500 to 4450 psi at a temperature of 140-262°C 300 grams of 29-EMS-70 were reduced using 30g. of copper chromite. Two hundred and eighty-four grams of reduced product, #29-EMS-72, was obtained from this procedure. This product is a clear colorless liquid having a Brookfield viscosity of 641 poise at 23°C.

The hydrogenolysis reaction is shown below:



This hydrogenolysis method is more amenable to scale-up than is the sequence of Raney Nickel hydrogenation followed by a lithium aluminum hydride reduction. We have analyzed the product by two different procedures to determine the hydroxyl equivalent weight. The first procedure is the infrared spectroscopic procedure based upon the use of neopentyl alcohol as a model compound as discussed in part A. This procedure gave an OH equivalent weight of 1226 for 29-EMS-72. The second procedure is based upon NMR spectroscopy using methyl benzoate as an internal standard added to the polymer solution in a known weight ratio to the amount of polymer present. From this weight ratio, and the relative areas of the $-\text{OCH}_3$ signal from methyl benzoate and the $-\text{OCH}_2-$ signal from the polymer end groups, the equivalent weight of the polymer can be directly obtained without resort to any calibration factor. This method gave an equivalent weight based upon the $-\text{CH}_2-\text{OH}$ groups of 1224.

Vapor pressure osmometry in chlorobenzene at 37°C gave a number average molecular weight of 2433. From these results we calculate a hydroxyl functionality of 1.99 for this product.

TABLE VI

ISOPRENE POLYMERIZATION 29-EMS-70

<u>Run No.</u>	<u>29-EMS-70</u>
<u>Charge Composition</u>	
Isoprene	60.57%
Benzene	37.71%
DEAB	1.72%
<u>Reaction Condition</u>	
Temperature Range	131-135°C
Pressure Range	900-1000 psi
Hold up Time	15-3 min.
Feed Rate	3718 g/hr.
Wt. Feed Used	3409 g
<u>Productivity</u>	
Yield	576 g.
Conversion	21.8%
Rate	491.5 g/hr.
<u>Properties</u>	
Specific Viscosity @ 80°C	0.054
Brookfield Viscosity @ 25°C	38.8 poise
Iodine No.	340
Ester Equiv. Wt., I.R.	1225
Appearance	Sl. yel. oil

Polyurethane cure formulations were then prepared on the above difunctional product. Toluene diisocyanate (TDI) and trimethylol propane (TMP) were used as the diisocyanate and triol components respectively. A 5% excess over the stoichiometric quantity of TDI was used in these cures which were done at 80°C in teflon lined molds of the type described in our last annual report, page 36. The resulting test bars were 2 inches long with a 3/8 inch square cross section and had metal end tabs (for attachment to the Instron test apparatus) bonded in place by the curing reaction. Two different cure formulations were used: (1) triol contributed 5% of the hydroxyl groups, (2) triol contributed 10% of the Hydroxyl groups. These formulations and the properties of the resulting test bars are summarized in Table VII.

In both cases tensile failure occurred in the rubber at a small defect (a bubble left in from the mixing operation) near the metal end tab. A layer of rubber remained bonded to the metal end tab showing that the adhesive strength developed by curing the formulations in contact with the steel bars was greater than the tensile strength of the rubber. This may be important in applications where good case bonding characteristics are required.

Approximately 250 grams of this product has been sent to J.P.L. for evaluation.

To provide an unsaturated diol product for comparison with 29-EMS-72, it was decided to use hydride reduction to reduce the ester end groups in 29-EMS-70 without saturating the polyisoprene chain. In this experiment, 10.6 grams (8.7 meq. ester) 29-EMS-70 was reduced using 0.34 grams (35.8 meq. hydride) lithium aluminum hydride in 80 ml diethyl ether. The reduced product, 9170-143-1, obtained in nearly quantitative yield, had a hydroxyl equivalent weight of 1226. Since the small quantity of material obtained from the hydride reduction was not put through the molecular still, it is most likely that a slightly higher level of low molecular weight diols such as 2,2,3,3,-tetramethyl butane diol (a known reduction product of diethyl tetramethyl succinate, an initiator-radical recombination product) accounts for this lower equivalent weight.

The reduced product was cured using toluene diisocyanate (TDI) and trimethylol propane (TMP) at 80°C for 67 hrs. using the formulation outlined in Table VIII.

The resulting test bar had a Shore-A hardness of 20. Uniaxial testing gave a value of 107 psi for the initial modulus, a yield strength of 27.5 psi at 70% elongation and a tensile strength of 56.5 psi at an elongation of 510%. Break occurred at a small bubble near the center of the bar.

TABLE VII

POLYURETHANE FORMULATIONS 1 AND 2 ON 29-EMS-72

Formulation	1	2
wt. 29-EMS-72, gms.	10.00	10.00
wt. TMP, gms.	.0192	.0406
wt. TDI, gms.	.786	.829
meq. OH from diol	8.16	8.16
meq. OH from triol	.429	.907
meq. OH Total	8.59	9.07
meq. NCO	9.02	9.52
r = meq. triol/meq. OH	.05	.10
R = meq. NCO/meq. OH	1.05	1.05
cure time, hrs.	63	63
cure temp., °C	80	80

Properties of Cured Formulations

Appearance	clear, colorless	clear, colorless
Shore A Hardness	24	28
Initial Modulus, psi	167	156
Yield Strength, psi	38.6	43
Yield Elongation, %	85	68
Tensile Strength, psi	75.8	63
Elongation at Break, %	1,025	310

TABLE VIII

POLYURETHANE FORMULATION USING UNSATURATED DIOL 9170-143-1

Formulation

wt. 9170-143-1	5.24	gms.
wt. TMP	.019	gms.
wt. TDI	.437	gms.
meq. OH from diol	4.70	
meq. OH from triol	0.43	
meq. OH Total	5.13	
meq. NCO	5.02	
r = meq. triol/meq. OH	.084	
R = meq. NCO/meq. OH	.98	
cure time, hrs.	67	
cure temperature, °C	80	

Properties After Cure

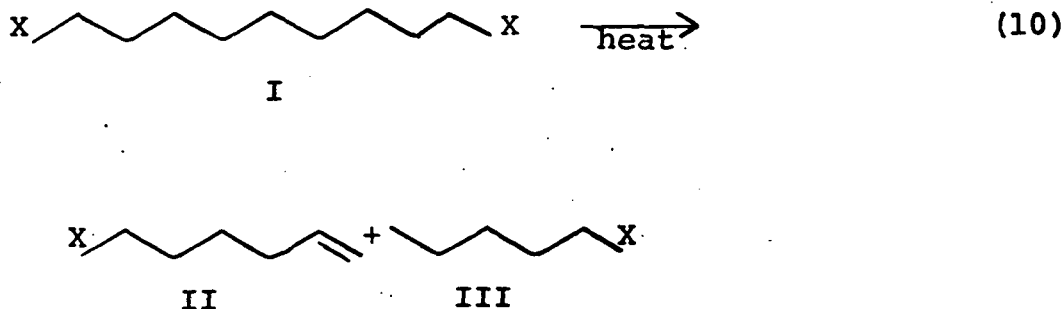
Appearance	Clear, Slight Straw Color
Shore A Hardness	20
Initial Modulus, psi	107
Yield Strength, psi	27.5
Yield Elongation, %	70
Tensile Strength, psi	56.5
Elongation at Break, %	510

Thin layer chromatography (TLC) was used to characterize and compare the diol products 29-EMS-72 (from 29-EMS-70 by hydrogenolysis) and 9107 -143-1 (from 29-EMS-70 by LiAlH_4 reduction). Four different solvent systems were used to develop the silica gel TLC plates upon which 50 and 100 μg spots of each of the diol polymers had been placed: a 1:1 mixture of hexane with benzene, pure benzene, a 1:1 mixture of benzene with chloroform and pure chloroform (listed in order of increasing eluting power).

These thin layer chromatograms showed only one component to be present in each of the two samples. In the 1:1 benzene-chloroform developed plate this component is observed as a uniform spindle shaped streak from $R_f = 0.1$ to $R_f = 0.6$. This elongation is due to the distribution of molecular sizes present in the samples. Lower molecular weight molecules of a given functionality type are more strongly adsorbed and hence have lower R_f values by virtue of their greater polarity. This is generally a lower order T. L. C. effect than R_f differences caused by different numbers of polar groups per molecule or differing polar group character, however, it generally is what limits the resolution of T. L. C. as applied to polymers.

No other component, corresponding for example to non- or monofunctional polymer, could be detected on any of the plates.

To further reduce the possibility that monofunctional polymers were present in 29-EMS-72 but not sufficiently resolved to permit identification, a small quantity (~ 0.5 g) of 29-EMS-72 was heated under a stream of nitrogen in a test tube over a bunsen flame until destructive distillation of the liquid polymer began to occur. At this point, heating was discontinued and the polymer (still a clear colorless liquid) allowed to cool under the nitrogen atmosphere. This "destructive distillation" results in the pyrolytic cleavage of some of the chains as shown below:



Thus if I is a difunctional molecule, one chain scission results in the formation of two monofunctional molecules, II and III. Subsequent chain scission of II or III results in the formation of non-functional molecules as well.

T. L. C. analysis of this pyrolyzed 29-EMS-72 clearly showed all three components, well resolved on the plate, thus demonstrating that if 29-EMS-72 had contained a mono or non-functional component, it should have been detected by our analysis.

We conclude from the T. L. C. studies, the functionality measurements and the results of the curing studies that both 29-EMS-72 and 1970-143-1 are telechelic diols and that the ester terminated precursor 29-EMS-70 is a telechelic diester.

C. Molecular Weight Distribution of 29-EMS-72 by Gel Permeation Chromatography.

In section A we described the preparation of a sample of hydroxy-telechelic liquid hydrocarbon polymer, 29-EMS-72. This saturated difunctional product was obtained via copper chromite catalyzed hydrogenolysis of 29-EMS-70, an ester-telechelic polyisoprene. Because of the preponderance of the 1-4 mode of free radical polymerization (~90%), the saturated product resulting from the hydrogenolysis was essentially an alternating 1:1 copolymer of ethylene with propylene with a minor contribution of more branched structures derived from 1-2 and 3-4 polymerized isoprene residues. This composition is responsible for the lower glass transition temperature ($T_g = 59^\circ\text{C}$) and lower Brookfield Viscosity (641 poise at 23°C) of 29-EMS-72 as compared with saturated polyisoprenes which had been obtained previously.^{2,3} The latter products had a high content of 1-2 and 3-4 polyisoprene due to the anionic polymerization methods used and upon hydrogenation were converted to extremely viscous liquid² (up to 20,000 poise Brookfield Viscosity) or semi-solids.³

We have examined 29-EMS-72 by gel permeation chromatography to determine whether a broad molecular weight distribution was produced by the free radical polymerization method used. The gel permeation chromatographic (GPC) system we used has been described in detail in our third quarterly report.⁴ The system we used then has since been upgraded to include an analogue-to-digital converter and a paper tape punch. As the

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- 2) D. E. Johnson and A. J. DiMilo, "The Development and Evaluation of a Hydrocarbon Binder for High Energy Solid Propellants." AFRPL-TR-66-40, Feb., 1966.
 - 3) K. Haejaski and C. S. Marvel, J. Pol. Sci., Part A, Vol. 2, pp. 2571-2594 (1964).
 - 4) A. C. Ashcraft, J. E. Potts, E. M. Sullivan, E. W. Wise, "Saturated Hydrocarbon Polymeric Binder for Advanced Solid Propellant and Hybrid Solid Grains", 3rd Quarterly Report, May 1 to July 31, 1966.

chromatogram is being recorded on a strip chart recorder, digital data of peak height vs. retention volume are simultaneously recorded on paper tape for later computer processing.

The first step in processing the raw chromatogram is to correct for baseline drift and normalize to constant maximum peak height. Figure 4 shows the processed chromatogram obtained. The vertical axis is a measure of relative concentration as determined by the differential refractometer used as a detector and the horizontal axis measures retention volume in "counts" of approximately 5 ml each.

The column configuration had previously been calibrated using National Bureau of Standards polystyrene samples of known molecular weight and having very narrow molecular weight distributions. Figure 5 shows the calibration curve obtained. The vertical axis measures "extended chain length" calculated for each standard sample by dividing the known $\bar{M}_n$ by the weight per Angstrom length of an extended polystyrene chain. The horizontal axis is a measure of the retention volume, again in 5 ml "counts", at which the given standard was eluted from the column.

When this information is processed along with a digitized G.P.C. curve, one can transform the original chromatogram into a molecular size distribution curve, which to all practical purposes is identical with a true molecular weight distribution curve. This curve, in integral form, is shown for the sample 29-EMS-72 in Figure 6. From this figure one immediately can see that 29-EMS-72 has a comparatively narrow molecular weight distribution: 90% of the sample was eluted over a retention volume range corresponding to 40 to 450 angstroms extended chain length.

Calculating the averages in the usual manner⁴ we found that the number average chain length was 105 angstroms and the weight average chain length was 182 angstroms, resulting in a weight to number average ratio of 1.73. And further, by noting that the $\bar{A}_n$ of 105 A corresponds to an $\bar{M}_n$ of 2433 (as determined by osmometry), we arrive at the conclusion that 90% of the polymer has a molecular weight between 1000 and 10,000.

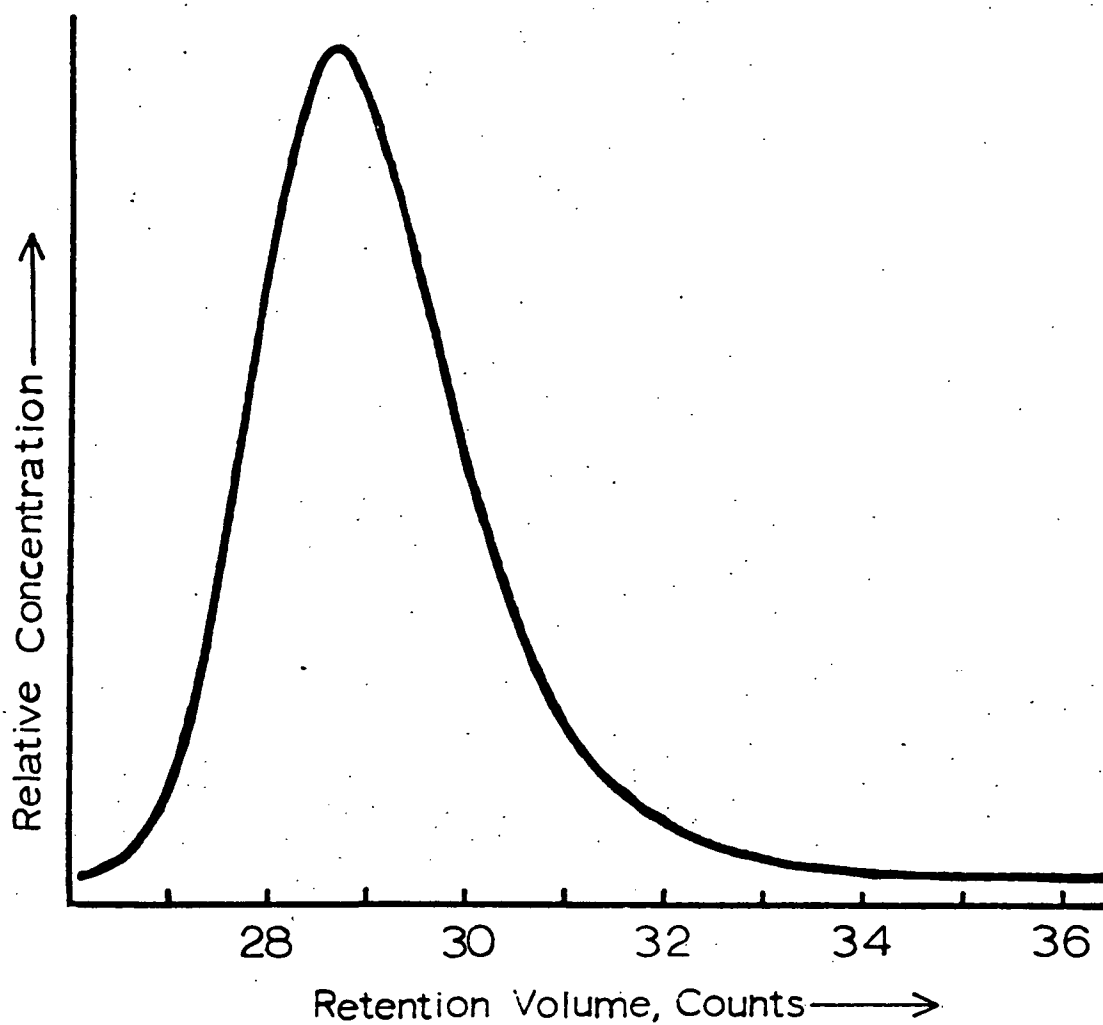


Fig.4. Baseline-Corrected Gel Permeation Chromatogram of 29-EMS-72

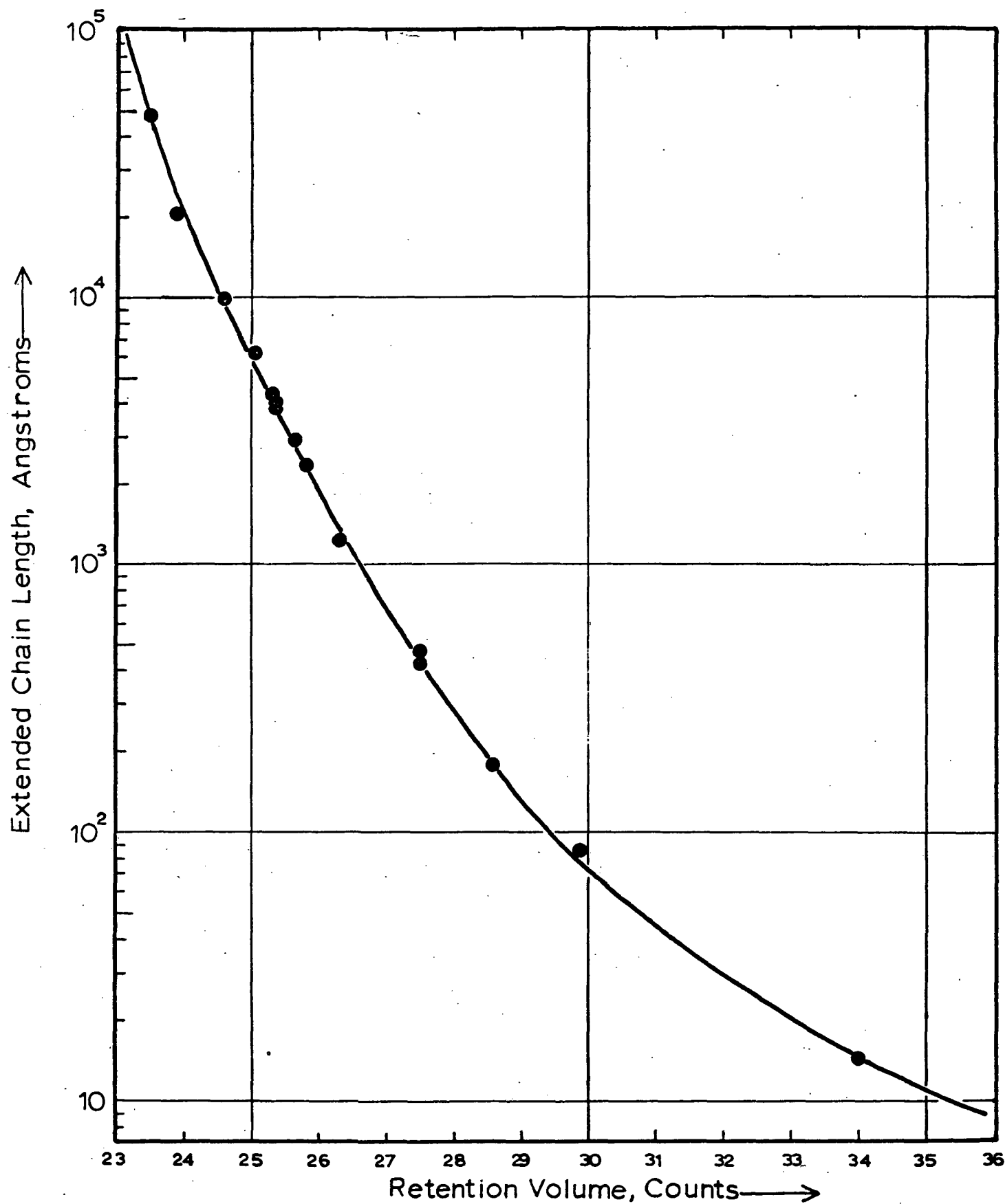


Fig.5. G.P.C. Column Calibration Curve

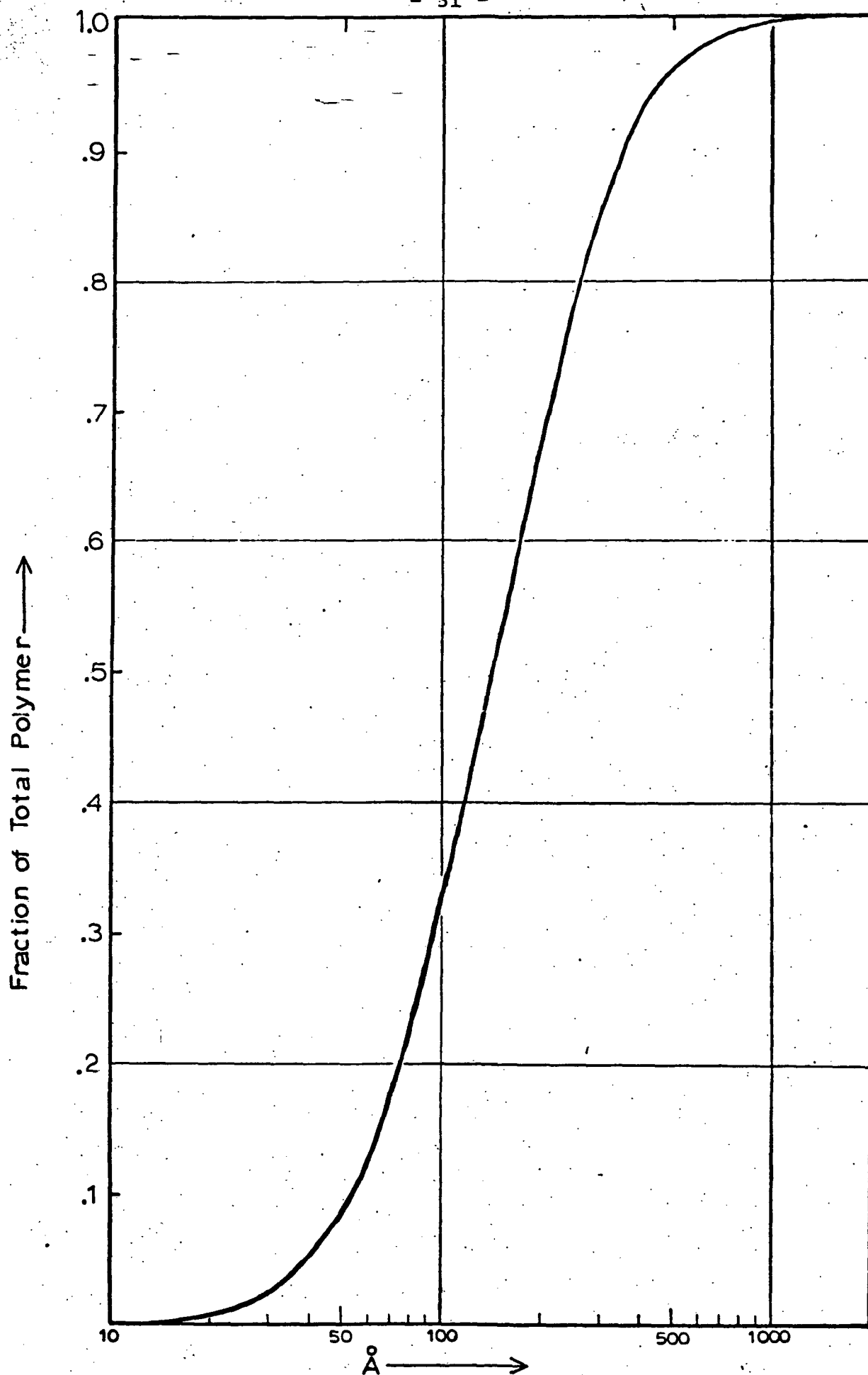


Fig.6. Integral Chain Length Distribution, 29-EMS-72 3

V. TECHNICAL DISCUSSION, PART 3 -

POLYISOPRENE PREPOLYMERS CONTAINING TERMINAL HYDROXYL GROUPS

A. Preparation of Hydroxy-Telechelic Polyisoprene

Since our current route to a saturated telechelic hydrocarbon prepolymer is based upon an intermediate ester-telechelic polyisoprene, we have the capability of preparing unsaturated telechelic prepolymers as well as saturated ones if a chemical transformation other than hydrogenolysis is used for endgroup conversion. This was demonstrated when the ester telechelic polyisoprene 20-EMS-70 was converted into the unsaturated diol 9170-143-1 as reported in section. Because of this capability, the scope of our program was expanded to include an investigation of the unsaturated prepolymers as well as their hydrogenated derivatives.

Accordingly, we prepared and submitted to J.P.L. for evaluation, two samples of hydroxy-telechelic polyisoprene.

The first sample, 9170-117-2, will be referred to as "Sample A" in the remainder of this discussion and the second sample, 9528-54-6, will be referred to as "Sample B". Table I summarizes the conditions used in the preparation of these samples, the workup procedures employed and the results of the characterization of the samples.

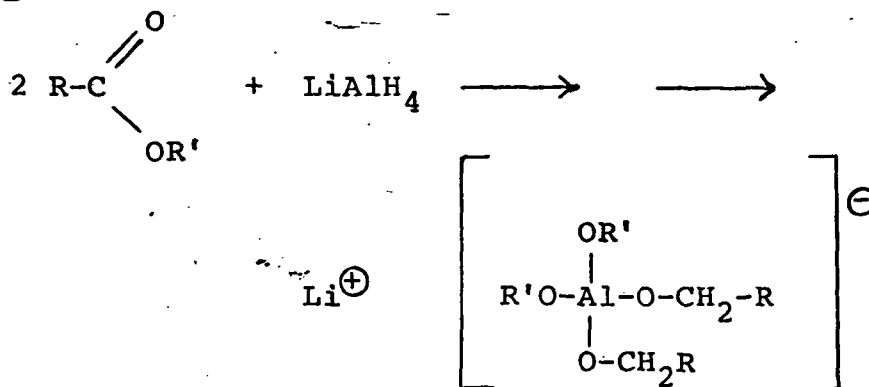
As outlined in the table there are major differences between the two samples, both in the methods of preparation and in the character of the samples themselves. The ester terminated precursor to sample A was prepared in a batch reactor under conditions selected to produce a 2000 to 3000 molecular weight material. All of the product remained in the reactor for the full 3.58 hours duration of the run. On the other hand the ester terminated precursor to Sample B was prepared in a continuous reactor under conditions selected to produce a product with a molecular weight near 1000. Since product was continually being discharged from the reactor as monomer and initiator were charged, the average residence time of the product in the reactor was much shorter than the total run duration, in this case, 15 minutes.

There were important differences in the lithium aluminum hydride reduction procedures employed to reduce the ester terminated polyisoprenes. The reduction leading to Sample A was run before the tetrafunctional nature of the reaction product of an ester with the exact stoichiometric quantity of hydride was fully appreciated:

TABLE I
SUMMARY OF CONDITIONS AND PROPERTIES

<u>Sample</u>	<u>A</u>	<u>B</u>
<u>Polymerization</u>		
Notebook Ref.	8908-122-4	30-EMS-18
Reactor	5 gal. Batch	1.5l., continuous
Temperature	97-101°C	134-137°C
Pressure	64-70 psi.	1000-1150 psi.
Isoprene used	4288 g.	5950 g.
DEAB used	159 g.	736 g.
Workup Applied	Stripping, 80°C/30mm. Counter current Extraction, Molecular Distillation	Stripping, 150°C/3mm.
Yield Polymer	1204 g.	3348 g.
M _n (V.P.O)	3000±150	1280±50
Ester Eq. Wt. (IR)	1300	680
Estimated Functionality*	2.2±.1	1.9±.1
Character	Cloudy liquid	Clear liquid
Brookfield Viscosity	73 poise/25°C	9.8 poise/25°C
<u>Reduction to Diol</u>		
Notebook Ref.	9170-117-2	9528-54-6
Reducing Agent	LiAlH ₄	LiAlH ₄
H ⁻ / Ester ratio	3.6:1	8:1
Method of Addition	H ⁻ added to Polymer by Extraction Method	Polymer added to H ⁻
Reaction Time	95 hours	4 hours 45 minutes
Workup Applied	Hydrolysis/aq. NH ₄ Cl soln Stripping, 80°C/30mm. Molecular Distillation at 105°C/0.15mm.	Hydrolysis/aq. NaOH Stripping, 80°C/30mm. Molecular Distillation at 178°C/0.7mm. Antioxidant added
Yield Reduced Polymer	570 g. from 645 g.	1630 g. from 2178 g.
M _n (VPO)	2415±177	1230±30
Hydroxyl Equiv. Wt.	1410 (IR)	696 (IR), ±2 by Acetylation
OH Functionality	1.71±.13	2.04±.06
Character	Cloudy liquid	Hazy, lt. Straw liquid
Brookfield Viscosity		21 poise/25°C

* The functionalities shown for the ester terminated products are to be regarded as estimated only because of the inaccuracies in the infrared method used.



When R is a polymer chain having another ester group on the other end, the structure shown above is polymeric itself. This fact, together with the tendency of ionically charged polymers to associate, resulted in the complete gellation of our reaction mixtures when hydride reduction was attempted on the telechelic diester precursor of Sample A. The problem was compounded by the method used for introducing the hydride into the reaction mixture: the hydride was extracted from a fritted glass bottomed thimble by refluxing solvent which drained back into the reaction flask containing the polymer and solvent. When a critical amount of hydride had been extracted, gellation occurred and further reaction was greatly impeded by the difficulty of properly stirring the reaction mixture. This necessitated very long reaction time to completely reduce the polymer.

Subsequent reductions, including the one leading to Sample B, were run by adding the polymer in ether solution to a refluxing reaction mixture of a large molar excess of hydride in ether. This procedure was simpler to carry out in practice and completely avoided the problem of gellation. The reaction was found to be nearly instantaneous and quantitative. We routinely refluxed the reaction mixtures for a few hours after the addition was complete, just to be sure of complete reaction.

The products from the hydride reductions were routinely run through the molecular still to insure the removal of all volatile materials. When Sample B was devolatilized in this manner, approximately 0.7% of tetramethylbutanediol (TMBD) was isolated. TBD is a readily sublimed white crystalline solid which results from the hydride reduction of the radical recombination product from DEAB. Its presence in the precursor to Sample B is directly related to the high DEAB concentration necessary to prepare a low molecular weight polymer. Except for a possibly adverse effect on Tg, TBD should not cause any difficulty in achieving a well cured rubbery binder material. However, it was virtually eliminated as a component in Sample B by the molecular distillation step as shown by our thin layer chromatographic analyses.

Functionality characterization of Samples A and B was done using V.P.O. molecular weight data (11 point determination on Sample A, 15 point determination on Sample B) and endgroup equivalent weight data obtained by infrared spectroscopy with neopentyl alcohol as reference (both samples) and our micro-acetylation procedure (Sample B only). In addition to the average functionality determinations, thin layer chromatography was employed to provide a qualitative check on the functionality distribution. These analyses confirmed the conclusions implied by the functionality determinations: Sample A contains a monofunctional fraction, Sample B does not. Neither sample contains any nonfunctional material and both appeared to contain on the order of 1% of a highly polar component which is not tetramethylbutanediol. The latter compound was not a significant contaminant in either sample and was presumably effectively removed by the molecular distillation step.

The three Appendices to this section contain a detailed account of the preparation of Sample A (Appendix 1), the preparation of Sample B (Appendix 2) and thin layer chromatographic study just completed in which both samples were analyzed and compared (Appendix 3).

APPENDIX 1

THE PREPARATION OF SAMPLE A

Sample A (9170-117-2) originated as a batchwise polymerization in the 5-gal. stirred autoclave reactor. This polymerization (run #8908-122) was run at 97-101°C under autogenous pressure (64-70 psi.). The reactor was initially charged with 4.288 kg. freshly distilled isoprene, 15.6 g. DEAB and 224 g. benzene. After purging the reactor with nitrogen, it was sealed and taken up to the operating temperature and pressure. At this point DEAB feed was started at a rate of about 40 grams per hour. It was pumped into the well stirred reactor as a 10% solution in benzene. After feeding the initiator for 3.58 hours the polymerization was terminated by turning on the internal cooling coils, and discharging the reactor contents into the receiving vessel. At this point the unreacted isoprene and most of the benzene were removed on a rotary vacuum evaporator and the crude product redissolved in heptane saturated with methanol to give a 10% solution. This was passed through a rotating disk column (R.D.C.) which had been set up as a countercurrent extractor using heptane and methanol as the two phases. The unreacted DEAB and its decomposition products were extracted into the methanol phase by this process. The heptane phase effluent from the R.D.C. was then concentrated on the rotary evaporator to give the purified liquid polymer which was devolatilized by passing through a wiped film molecular still at 100°C/3mm.

The refined product was recovered as 1.204 kg. of a slightly cloudy straw colored oil, Brookfield viscosity 73 poise at room temperature, 2 poise at 80°C. A preliminary estimate of the functionality of this ester terminated polyisoprene was obtained from a four point V.P.O. M_n determination of 3000 ± 150 (chlorobenzene, 37°C) and the ester equivalent weight of 1300 (determined by I.R. spectroscopy, ethylpivalate used as reference). These measurements implied an ester functionality of about 2.2 with an uncertainty of about 0.1.

Examination of the above material with a phase contrast microscopy at 1000 x disclosed the reason for the cloudy appearance. An incompatible liquid phase was present amounting to about 1 volume % in amount. This phase existed as spherical droplets $\frac{1}{2}$ to 2 microns in diameter having a lower refractive index than the bulk of the liquid present. Acetone extraction of 7.5 g. gave 0.5 g. of a yellow oil extract which appeared to contain the incompatible fraction since the acetone insoluble phase had become clear. The extract was apparently a low molecular weight fraction of high ester content as shown by its infrared spectrum equivalent wt. 547 based upon ethyl pivalate, and nuclear magnetic resonance spectrum. The NMR spectrum clearly showed a quartet near 4 ppm due to the ethyl ester endgroup. Calculation of the equivalent wt. of the extract using the area of this signal gave a value of 603, 1.1 times the value as determined by IR.

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Lithium aluminum hydride was then used to reduce 645 grams of the ester terminated product. The technique employed was different from that currently used. Instead of adding the polymer to an excess of hydride, we refluxed an ether solution of the polymer in a Soxhlet type extractor having 18.29 grams of lumps of hydride in the cup. Refluxing solvent leached out the soluble LiAlH_4 from the grey lumps leaving the oxide and other inorganic impurities behind. This results in a very "clean" reaction mixture: a clear colorless liquid. However, when the critical stoichiometric amount of hydride had been extracted and reacted with endgroups, the entire reaction mixture set up into a gelled mass which gathered into an intractible lump of gum rubber around the mechanical stirrer. Needless to say, this prevented the reaction from going to completion. After decomposing the excess hydride and the gelled aluminate crosslinked polymer by hydrolysis we recovered 606 grams of liquid polymer after extraction, washing and evaporation of solvent. Infrared spectroscopy showed hydroxyl to be present, however, the ester absorption was still very strong showing that about 1/3 the original groups were still present.

The recovered partially reduced polymer was again subjected to LiAlH_4 treatment, however, on this second attempt, reflux was continued after the gel had formed, allowing a excess of hydride to build up in the pot. When this was done we found that the gel gradually dissolved, eventually reverting to a stirrable liquid reaction mixture. In the second attempt 9.55 gms. of hydride were used and the total reaction period was 95 hours. After workup we recovered 578 grams of liquid product showing no trace of the original ester absorption and having a strong hydroxyl absorption at 3450 cm^{-1} .

The reduced product was then passed through the falling wiped film molecular still at $105^\circ\text{C}/0.15\text{ mm.}$ to give the final product 9170-117-2 (Sample A) which we sent to J.P.L.

We estimated the number average molecular weight from a four point V.P.O. determination (Chlorobenzene at 37°C) to be 2517 and used our infrared assay based upon neopentyl alcohol as a reference to measure the hydroxyl equivalent weight of 1410. From these values we calculate a functionality of 1.79. These values were the ones quoted in the letter of transmittal.

We later did two more four point determinations of the $\bar{M}_n$ of this sample giving eight additional points, one of which was discarded as a flier. From all eleven points points remaining we obtained a number average molecular weight of 2415 ± 177 by a least squares fit of the osmometer data to a quadratic equation of the form: $\Delta R = A_1 C + A_2 C^2$, (where A_1 is the slope of the parabola

as it goes through the origin of the ΔR versus C plot.) From this parameter and a machine calibration factor the M_n is calculated. This new value lowers the calculated average functionality to 1.71 with an estimated standard error of ± 0.13 .

As indicated in the letter of transmittal, thin layer chromatography showed one major component, presumably difunctional from its R_f value, and a minor component having a higher R_f value appropriate for a monofunctional fraction. No nonfunctional material was present. The streaks were rather elongated and overlapped on the plate, possibly indicating a broad molecular weight distribution.

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5. The molecular weight determined above for Sample A is at variance with the results of gel permeation chromatography as well as a repeat of the V.P.O. determination. These results give a value near 2900 and imply that Sample A is actually near 2 in functionality. See Section E.
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APPENDIX 2

PREPARATION OF SAMPLE B

Sample B (9528-ACA-54-6) originated as a polymerization in the 1.5l. continuous stirred autoclave reactor (the "Unit-II" reactor). This polymerization was run at 134-137°C and 1000-1150 psi. (nitrogen pressurized) for a steady-state period of 2.68 hours. The hold up time in the reactor was 15.08 minutes at the feed rate employed of 3.842 kg. per hour. The feed composition was 57.73% isoprene, 34.87% benzene and 7.40% DEAB by weight. A total of 10.307 kg. of feed was used over the ~68 hours steady-state period. The continuously discharged product was collected in a product receiver blanketed with nitrogen. At the end of the run the polymer was recovered by stripping off the unreacted monomer and the benzene solvent on the rotovac. At least partial removal of the initiator decomposition products was effected by a final heating to 150°C under 3 mm. pressure, however, this treatment is not as thorough as the molecular distillation step used routinely on all our final products.

The polymer was recovered as 3.348 kg. of a clear yellow oil having a Brookfield Viscosity of 9.8 poise at 25°C. The molecular weight was found to be 1280 ± 50 by V.P.O. in toluene at 37°C. Combining this result with the ester equivalent weight of 680 estimated by I.R., we calculated a functionality of $2.0 \pm .1$ for thsi product, 30-EMS-18.

In a preliminary reduction experiment (9528-52) we placed 23.88 grams (0.60 moles, 2.4 eq.) 95% lithium aluminum hydride in crude lump form in a 5 liter, 3-necked, round bottomed flask fitted with efficient water cooled condenser, addition funnel and mechanical stirrer. The flask had previously been swept out with a nitrogen atmosphere. 1500 ml absolute ether was then added and the hydride/ether mixture mechanically stirred. At this point a solution of about 500 ml (398.94 g., ~.59 eq. ester) 30-EMS-18 was prepared in 50 ml absolute ether. This solution was added dropwise with stirring to the reaction vessel containing the hydride. In addition rate of ~25 ml/min. resulted in a steady exothermic reaction maintaining reflux of ether due to the heat of reaction about $\frac{1}{4}$ way up the reflux condenser. About 45 minutes were required to add all of the polymer solution. No gellation occurred at any point since a two-fold excess of LiAlH_4 was used. After addition of all the polymer was accomplished the reaction mixture was stirred under gentle reflux (external heat applied using a heating mantle at this point) for 4 hours.

At this point the excess hydride and the polymeric aluminate were decomposed by an improved hydrolytic procedure: 24 ml of H_2O was added (cautiously, dropwise with stirring - large volumes of H_2 and ether vapor come off at this point - hood mandatory), followed by 24 ml of 15% aqueous sodium hydroxide and finally 75 ml H_2O , all added dropwise with stirring. During the initial stages of the hydrolysis the reaction mixture stiffened to the consistency of a paste and foaming was difficult to keep under control, however, after addition of the final quantity of water, the gray intractable hydride/polymer mixture abruptly changed to an easily stirred suspension of a white solid in a clear ether solution. When stirring was stopped, the white solid settled out cleanly permitting the easy decantation of the supernatant ether solution. Following this decantation, the solution and washings were dried over anhydrous sodium sulfate and the ether removed on the rotary evaporator. 352.8 grams of a hazy colorless oil resulted. Infrared spectroscopy showed the presence of a trace of ester absorption, however, the equivalent weight based upon this weak absorption was greater than 20,000, showing that over 95% of the ester groups had been reduced. Hydroxyl functionality was estimated from the infrared spectrum (neopentyl alcohol reference) in 25% ethyl acetate/ CCl_4 solution which gave a hydroxyl equivalent weight of 628, and the V.P.O. $\bar{M}_n$ of 1247 $\pm$ (4point measurement in Toluene at 37°C). The calculated functionality is 1.98.

Having had this preliminary experience with the hydride reduction of 30-EMS-18 we proceeded to reduce the bulk of the sample in lb. batches in experiment 9528-54. In these batches a still greater excess of $LiAlH_4$ was used to insure completion of the reduction of the ester groups. The standard "recipe" used in these five batch reductions was as follows: ~500 ml 30-EMS-18 dissolved in 500 ml absolute ether added to 50 grams hydride in 1500 ml absolute ether. Workup was with 50 ml H_2O , 50 ml 15% NaOH and 150 ml H_2O . Otherwise the procedures used were the same as those used in experiment 9528-52.

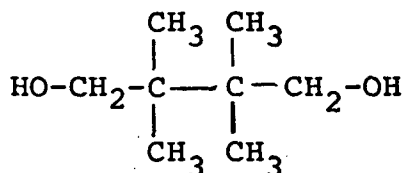
The modifications were successful in yielding a product containing no detectable ester absorption. Five batches in all were processed in this way: 9528-54-1 (413 grams yield), 9528-54-2 (418 grams yield), 9528-54-4 (348 grams yield), 9528-54-5 (323 grams yield). The lower yield in run 1 was due to a material loss (workup got out of control and foamed out of the flask!!), run 4 was based on a smaller quantity of 30-EMS-18 (384 g.) and run 5 was a rework of the product from experiment 9528-52.

All the batches were combined and passed through the molecular still operating at 178°C/0.7 mm pressure to give 1754 grams devolatilized product. To stabilize the product and inhibit oxidation 0.88 grams of ionol (di-t-butyl p-cresol) was added as an antioxidant using 600 ml pentane to insure complete mixing. At this point it was noted that a small quantity of a white

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crystalline substance was present in the pentane solution of the residue product from the still, as well as in the alembic of the still, and it was thickly encrusted on the cold finger of the still. Apparently a sufficient quantity of sublimate had collected on the cold finger of the still such that it was wiped off by the rotating wiper blades, normally separated by about 1/4" from the surface of the cold finger. The wiped off sublimate fell into the alembic and a small quantity fell all the way into the product receiver.

A small quantity was removed from the alembic and found to be quite insoluble in cold pentane. Accordingly the pentane solution of the devolatilized polymer was diluted with another 2000 ml of pentane, decanted from the solid material, cooled to 0°C and filtered to give a clear solution. The solid was recrystallized from 2½ to 1 heptane/ether and recovered as white crystalline needles having a camphoraceous odor. The N.M.R. spectrum established the structure shown below:



2,2,3,3-tetramethylbutanediol (TMBD)

TMBD is the LiAlH_4 reduction product of diethyl tetramethylsuccinate, the major decomposition product of DEAB.

The pentane was removed from the clear solution of the reduced polymer on the rotary evaporator. The residue was devolatilized by leaving it on the rotary evaporator under vacuum and rotating overnight while a slow stream of dry nitrogen was admitted to continually sweep out the evacuated flask containing the polymer. This resulted in the recovery of 1.63 kg of completely reduced and devolatilized liquid product, slightly hazy with a light straw color, Brookfield viscosity 1.4 poise/76°C, 21 poise/25°C.

A 15 point determination of the $\bar{M}_n$ by V.P.O. in toluene at 37°C gave a value of 1230 ± 30 . Infrared spectroscopy gave a hydroxyl equivalent weight of 696, however, direct determination of the hydroxyl equivalent weight by our acetylation and non-aqueous titration procedure (3 samples used) gave a value of 605 ± 2 which we believe to be a more accurate assay of hydroxyl content. The latter equivalent weight and the $\bar{M}_n$ lead to a calculated average functionality of 2.04 ± 0.06 . The limits of 1.98 to 2.10 on the functionality are combined result of the ± 30 on the $\bar{M}_n$ calculated from the standard error of estimate of the least squares fit of the V.P.O. data and the ± 2 on the acetylation equivalent weight

which was the estimated standard deviation of the average of three determinations (actual values: 606.3, 602.7, 604.5).

We then analyzed the final product ("Sample B") by thin layer chromatography on silica gel plates. Four different developing solvents were used on five separate plates, one of which was deactivated, to resolve as well as possible all probable constituents: 1)1:1 Benzene/Heptane, 2)100% Benzene, 3)1:1 Chloroform/Benzene, 4)100% Chloroform and 5)100% Chloroform on a plate which was deactivated by immersion in methanol containing 1% H₂O and drying. Plate 1), which would have shown the best development of nonfunctional impurities, showed nothing whatever past $R_f = 0.1$. Plate 2) which would have shown the best development of a monofunctional fraction, showed nothing past $R_f = 0.4$. The applied polymer spots partially developed as elongated teardrop shapes stretching from the origin to $R_f = \sim 0.3$ with faint development out to $R_f = 0.4$. No indication of any resolution into separate components of differing functionality could be detected. Plate 3) is a good "compromise" plate which gives optimum separation between mono and difunctional components. No mono was detected. The difunctional polymer had almost completely left the origin on this plate and was displayed as an elongated spindle from $R_f = 0$. out to $R_f = 0.5$. Plate 4) gave the best development of the difunctional component. It stretched from a wisp of a tail just touching the origin, out to $R_f = 0.7$. No resolution of this smoothly tapering spindle shaped streak was detectable on the plate. At the origin a very small concentrated spot was left behind. At this time we had not established whether this was a higher functionality fraction or perhaps a trace of the TMBD not removed by the molecular distillation. In any event it was obviously a minor constituent of the polymer, amounting to a few percent at most of the total material made visible by the ammonium sulfate spray and char. The last chromatogram on the deactivated plate resulted in complete development of the major component. It appeared as a greatly elongated spindle from R_f of 0.1 to 0.9. The minor constituent remained at the origin as a very small compact spot, comparable in size to the end of the micropipette used to apply the sample to the plate.

While no sample of an authentic tri- or tetrafunctional polyisoprene is available to use as a reference, it is probable that such a material would have migrated to some extent on the deactivated plate developed with chloroform. Because of this, we presently believe that the $R_f = 0$. spot represents a trace contaminant of a highly polar material such as a polyol derived from one of the telomeric DEAB decomposition products. If this is the case it may be easy to remove by filtration through a short column of an absorbent such as silica gel or activated carbon. Preliminary experiments indicate that this is possible.

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APPENDIX 3THIN LAYER CHROMATOGRAPHIC STUDY

To provide a better comparison between Samples A and B and to determine whether the diol TMBD was present in either, we conducted a T.L.C. study in which Sample A, Sample B and TMBD were all spotted on the same plates and developed with a series of solvents.

A problem was encountered immediately when we discovered that TMBD failed to char and yield a visible spot when sprayed with aqueous ammonium sulfate and heated. This behavior is understandable in view of the fact that TMBD is saturated, has no tertiary hydrogens and is structurally incapable of undergoing dehydration. The photograph of "Plate A" in Figure 7 shows the appearance of our first T.L.C. plate in this study. Spots 1 through 5 were respectively: 100, 20, 10, 2 and 1 microgram spots of TMBD. No charring at all was visible on the oven baked plate, however, when the plates were wet after spraying with the reagent, TMBD was visible as white spots, $R_f \sim .05$, because of the differing refractive index relative to that of water.

Spot 6 on plate A was 200 micrograms of Sample A. Spots 7 through 10 were 200 micrograms each of the individual batches later composited and molecularly distilled to give Sample B, and spot 11 is 200 micrograms of Sample B. Note the uniformity and absence of low functionality components in Spots 7-11. Monofunctional polymer of this molecular weight would have resulted in a streak from about $R_f = .3$ to $.6$ and nonfunctional polymer would have followed the solvent front up the plate. Spot 6 shows the combined effects of higher molecular weight, broader molecular weight distribution (from the batchwise polymerization) and an average functionality less than 2. On the original plate a weak boundary can be seen at $R_f = 0.5$. This may mark the region where the high molecular weight portion of the difunctional fraction overlaps the low molecular weight portion of the monofunctional fraction.

Plate B shows the effect obtained when a 1% KMnO_4 solution was sprayed on the T.L.C. plate just discussed. The greater oxidizing power of KMnO_4 on the acidic plate resulted in a weak visualization of the TMBD in Spot 1, just visible as an oval patch from $R_f = 0.$ to $.05$.

Plates C and D were visualized by spraying with a 1% solution of KMnO_4 in 5% aqueous sulfuric acid and taking a photograph through a Wratten 35 filter (purple, makes KMnO_4 invisible) before the plates could fade. The places where KMnO_4 (purple) was reduced to MnO_2 (brown) show up as dark areas and regions where the MnO_2 was further reduced to the less colored manganous ion,

the plate appears white. The latter regions are most noted in the central high concentration regions of a streak or spot.

The spots on plate C are: 1 through 7 are 40, 20, 10, 5, 2, 1 and $\frac{1}{2}$ micrograms of TMBD respectively (Note that all but spot 7 are readily seen as white spots on the photograph. On the original plate even spot 7 could be seen as a minute white spot). Spots 8, 9 and 10 are 400, 200 and 100 micrograms of Sample B respectively and spots 11, 12 and 13 are the same amounts of Sample A. You will note that the R_f of TMBD is definitely greater than zero under these conditions, approximately 0.02 to 0.05, depending on the concentration. Both Sample A and Sample B, on the other hand contain, a component that does not migrate at all. This is the very minor impurity of high polarity previously noted in the earlier T.L. C. studies on Sample B.

Plate D shows that no significant quantity of TMBD is present in Sample B. The higher polarity developing solvent results in an R_f of 0.13 to 0.2 for TMBD is spots 1 through 5 contain respectively 200, 100, 20, 10 and 2 micrograms of TMBD. Spots 6 through 8 are 200, 400, and 600 micrograms respectively of 9528-54-1, one of the batches composited to give Sample B. This batch had not been subjected to molecular distillation and therefore contains all the TMBD produced in the reaction. Note the dark spot at $R_f = 0.13$ in all three chromatograms. The spot intensity at $R_f = 0.13$ in 6 is comparable to that in 5 which represents 2 micrograms of TMBD. Therefore 9528-54-1 contains approximately $2\mu\text{g}/200\mu\text{g}$ or $\sim 1\%$ of TMBD. (Note that 12 grams, or 0.7% by weight, of TMBD was isolated from the molecular distillation yielding 1750 grams of Sample B.)

Spots 9, 10, and 11 of Plate D are of 200, 400 and 600 micrograms of Sample B respectively. Note that the TMBD spot at $R_f = 0.13$ does not appear in these chromatograms. The final chromatogram on Plate D is the result of applying 40 micrograms of TMBD and 200 micrograms of Sample B at the same position on the plate.

We can make a very rough estimation of the amount of the highly polar fraction of $R_f = 0$ which both Sample A and Sample B apparently contain by noting that the component at $R_f = 0$ on spot 6 of plate D is slightly less intense than the $2\mu\text{g}$ spot #5 of TMBD. This result implies that the concentration of this material in Sample B is less than 1%. Note that the heavier spots of TMBD on Plate D also show this $R_f = 0$ component. This finding supports the view that the zero R_f component is a small highly polar molecule rather than a very high functionality polymer fraction since all the material comprising the TMBD spots has been distilled.

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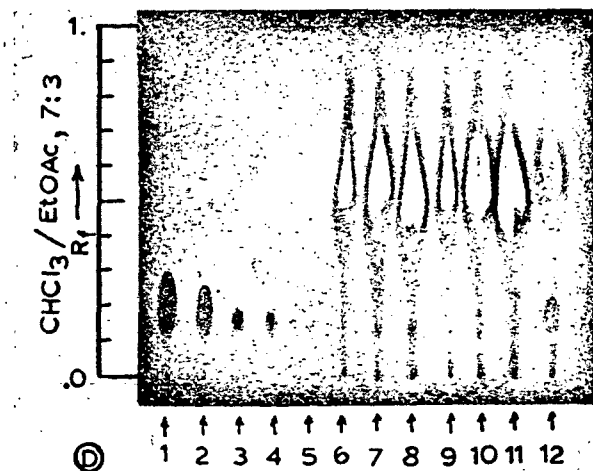
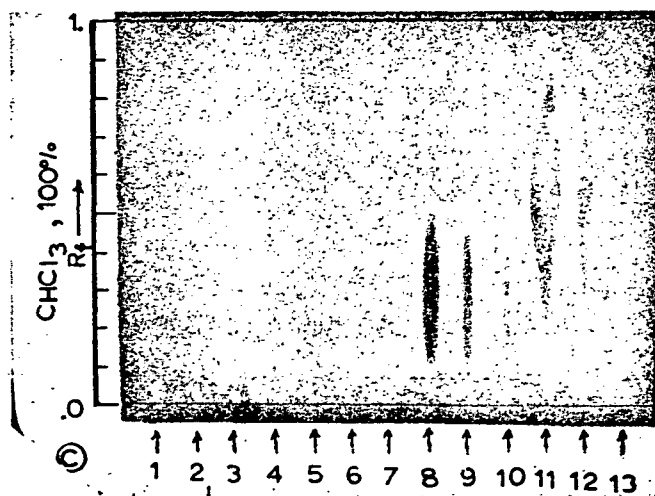
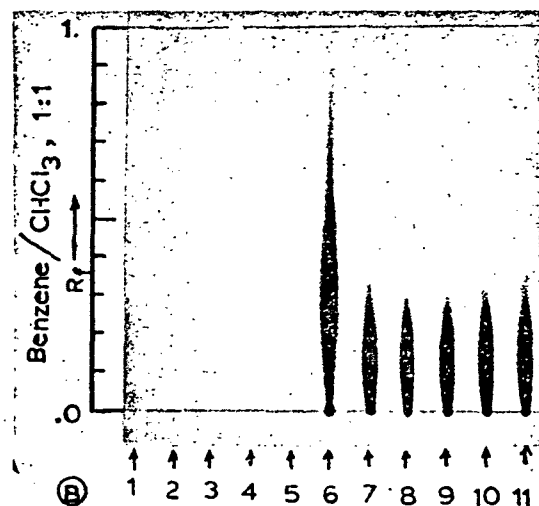
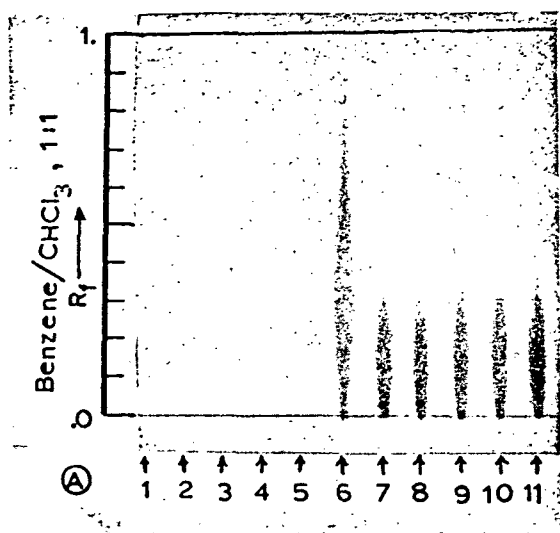


FIGURE 7

THIN LAYER CHROMATOGRAPHY OF SAMPLES A&B

B. The Preparation of Ester-Telechelic Polyisoprenes in the Continuous Reactor

The 1.5 liter Unit II continuous stirred autoclave reactor⁶ was used to prepare two samples of liquid polyisoprene using diethyl azobisisobutyrate (DEAB) initiator. A premixed feed solution was prepared using isoprene (distilled to remove inhibitor), DEAB and benzene as solvent. This was pumped into the heated reactor at a constant rate. When the reactor was hydraulically filled, the discharge valve was throttled by the control system to maintain the system pressure within a preset range. After approximately 4 reactor volumes of the feed solution had passed through the reactor, and the pressure and temperature readings had stabilized, it was considered that steady state conditions had been attained. From this point on for the duration of the run, the discharged reactor product was retained in a separate receiver for recovery of the polymer. This was accomplished by vacuum stripping to remove benzene and unpolymerized isoprene.

The table on the next page summarizes the reaction conditions during the steady state portion of the two runs, and describes the properties of the polyisoprenes obtained.

All the product from Run No. 30-EMS-22 was collected in a single product receiver and recovered as 2.63 kg. of a light straw colored oil. Analysis of this product by Vapor Pressure Osmometry in toluene at 37°C gave a number average molecular weight of 2150±70. Infrared spectroscopic analysis using ethyl pivalate as reference compound gave an equivalent weight of 1154.

The product from Run No. 54-EWW-2 was collected as three separate fractions corresponding to the beginning, middle and final portions of the steady state operating period. This was done to provide a check on the uniformity of the product produced during a continuous run. The molecular weight was determined on part 4 alone: 2460±30. Infrared spectroscopy provided estimates of the ester equivalent weight of the product from each part: 1463, 1518, and 1484 for parts 2, 3 and 4 respectively.

The variation in specific viscosity of ±.0015 about the average value of 0.0617 may be used to estimate the molecular weight variation which occurred during the run, provided one has correlated molecular weight with solution viscosity. This correlation, obtained from the data of nine previous runs, is shown in Figure 1. The specific viscosities were taken at 80°C in methyl cyclohexane solvent and the molecular weights were obtained by vapor pressure osmometry in toluene at 37°C. An approximate fit to a straight line was obtained on the log-log plot corresponding to the equation:

$$\eta = 0.00213 M^{0.425}$$

6. Described on p 124 of our triennial report.

TABLE X

ESTER TELECHELIC POLYISOPRENE

Run No.	30-EMS 22	2-2	55-EWW 2-3	2-4
Feed Composition, Wgt. % on TC				
Isoprene	60.13	60.67		
Benzene	37.45	37.78		
DEAB(1)	2.42	1.55		
Total Feed Used, gms.	16,011	3,868	3,868	1,780
Reaction Conditions				
Temperature, °C	134-137	135	135	136
Pressure, psig	1000-1150	1100±50	1100±50	1100±50
Hold-up Time, min.	14.57	14.71	14.71	15.7
Operating Time, hr.	4.05	1.0	1.0	0.483
Ave. Feed Rate, gm/hr	3953	3,868	3,868	3,686
Productivity				
Yield, gms.	2632	487	520	291
Conversion, %	25.8	20.8	22.2	26.0
Prod. Rate, gms/hr.	613	487	520	593
Prod. Rate, lbs/cu.ft./hr.	25.8	20.5	21.8	24.9
Physical Properties				
Brookfield Viscosity, poise T°C	33.8 ²⁵	54.0 ^{21.8}	52.0 ^{21.8}	55.4 ^{21.8}
Specific Viscosity, 80°C	0.053	0.062	0.060	0.063
Solidification Temperature, °C	-70	-70	-70	-70
Description	Lt. Straw Oil	Colorless Oil	Colorless Oil	Colorless Oil

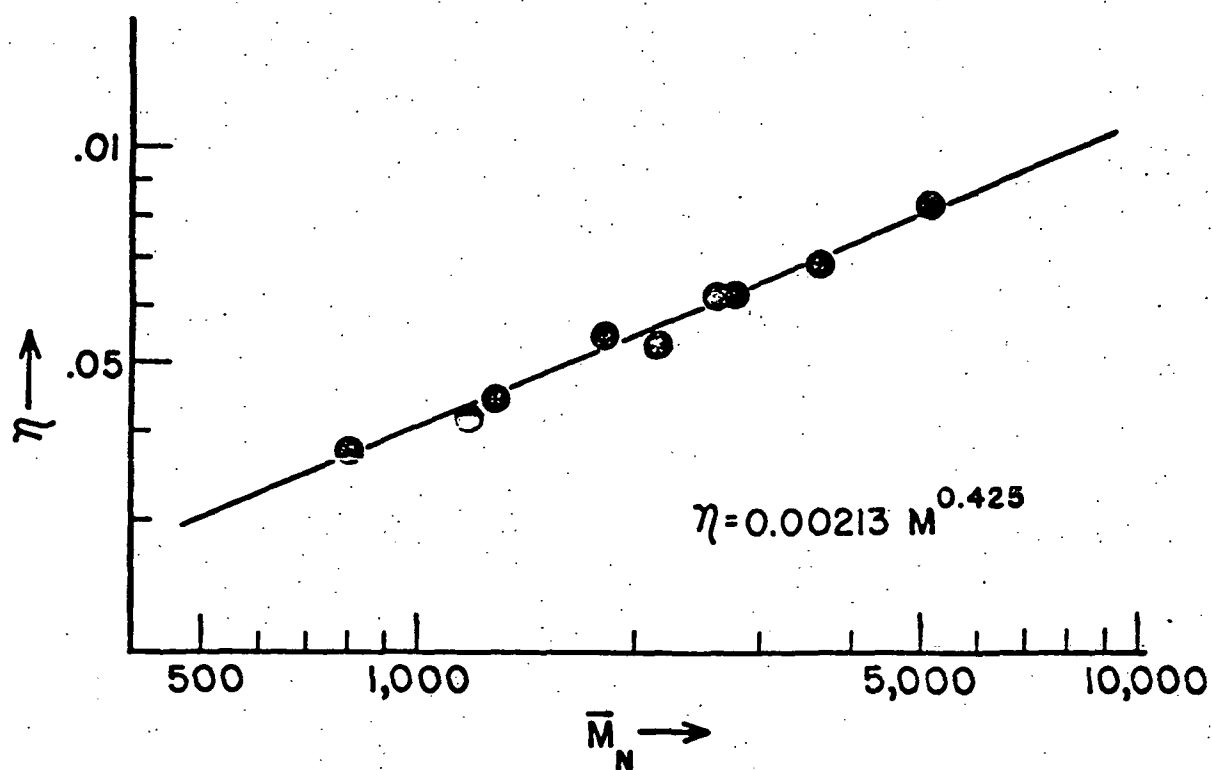


FIGURE 8. VISCOSITY-MOLECULAR WEIGHT RELATIONSHIP
FOR ESTER-TELECHELIC POLYISOPRENE

Using the above correlation, the variation in molecular weight during the course of the continuous polymerization was estimated to be ± 160 about the average value for the whole run. This was considered to be negligible in comparison to the probable width of the molecular weight distribution which would normally result from free radical polymerization under these conditions. Accordingly, parts 2, 3 and 4 of Run No. 55-EWW-2 were combined, saving a few grams of each as a reference sample.

C. The Preparation of Hydroxy-Telechelic Polyisoprene Samples "C" and "D"

1) Sample C

Into a 3-liter round bottomed flask fitted with mechanical stirrer, efficient condenser, addition funnel, bottom outlet and means for sweeping out with nitrogen was placed 25 grams (2.64 eq. H) lithium aluminum hydride and 1.2 liters absolute ether. To this was added, dropwise with stirring under an atmosphere of dry nitrogen, a solution of 512.7 grams ester-telechelic polyisoprene 30-EMS-22 in absolute ether. The total volume of this solution was 1.2 liters. The addition required 2 hours 10 minutes. After addition was complete the reaction mixture was stirred under gentle reflux for an additional 1 hour 45 minutes. At this point the reaction mixture was cautiously discharged in small portions, through the bottom outlet, into a well stirred 5-liter flask containing 125 ml. H_2O , 3.75 grams sodium hydroxide and 150 ml. ether. (This method of decomposing the excess hydride resulted in much improved control of foaming as compared with the previously used method where the aqueous caustic was added dropwise to the reaction mixture). After the entire contents of the reaction vessel had been discharged, the contents of the 5-liter flask were allowed to stand overnight and then filtered to recover the supernatant ether layer. This was evaporated to give 459 grams crude product.

The above procedure was also used to reduce another 300 grams 30-EMS-22. The combined crude product (731 grams) was dissolved in 1500 ml heptane to which 0.35 grams di-*t*-butyl-*para*-cresol (Ionol) had been added. This solution was dried over anhydrous magnesium sulfate, filtered and restriped to remove the heptane. The resulting oil was passed through the wiped film molecular distillation apparatus at $160^{\circ}C$ and 30 microns pressure to give 696 grams devolatilized hydroxy-telechelic polyisoprene. This product was cloudy oil having a Brookfield viscosity of 62.8 poise at $28^{\circ}C$, a number average molecular weight of 2225 ± 50 and a hydroxyl equivalent weight (by acetylation) of 1124 ± 15 for a calculated average functionality of 1.98 ± 0.07 .

Because of its cloudy appearance an additional purification step was used on this product. It was dissolved in an equal volume of pentane at room temperature to give an opalescent straw colored solution which was filtered under pressure through a Seitz S-3 filter pad (pore size 0.01 microns) to give a clear solution. After stripping off the pentane on the rotary evaporator, followed by evacuation for 12 hours under a stream of nitrogen, the sample was found to remain slightly cloudy in appearance. The Brookfield viscosity was 79.8 poise at 25°C. A recheck of the hydroxyl content by infrared spectroscopy gave an equivalent weight of 1103, within experimental error of the value determined prior to filtration by the more accurate acetylation procedure.

The properties of this hydroxy-telechelic polyisoprene, hereafter referred to as "Sample C" are summarized in Table XI.

2) Sample D

Into a 5-liter round bottomed flask fitted with mechanical stirrer, efficient condenser, addition funnel, bottom outlet, and nitrogen sweep was placed 63.5 grams (6.64 eq. H⁻) LiAlH₄ and 1500 ml absolute ether. To this was added, dropwise with stirring under an atmosphere of nitrogen, a solution of 1238.5 grams of ester-telechelic polyisoprene from the composite of 53-EWW-2-2,2-3 and 2-4. The addition was accomplished over a six hour period. During this time reflux was maintained by the exothermic reaction. It was necessary to add an additional 39.5 grams of LiAlH₄ in portions during the addition of the polymer to prevent excessive viscosity buildup as reduction proceeded. After all addition of reactants was complete, the reaction mixture was heated and stirred under gentle reflux for an additional hour and then allowed to stand under a nitrogen atmosphere at room temperature overnight. At this point the reaction mixture was cautiously added, dropwise with stirring, to a 12-liter flask containing 325 ml H₂O, 500 ml ether and 11-25 grams NaOH under a nitrogen atmosphere. The addition required 7½ hours. After all the reaction mixture had been added an additional 3.3 g. NaOH in 150 ml H₂O was added to complete the decomposition of the hydride and coagulation of the inorganic salts. This resulted in the formation of a clear supernatant ether layer and a white precipitate. The ether layer was recovered by filtration over anhydrous Na₂SO₄ and evaporated to give 1184 grams of a slightly hazy colorless liquid product. This was devolatilized by passage through the wiped film molecular still at 155°C and 100 microns pressure to give 1055 grams residue product, hereinafter called Sample D. The Brookfield viscosity of Sample D was 75.3 poise at 28°C. The number average molecular weight was 2454±154 and the hydroxyl equivalent weight was 1240±33 (by acetylation) for a calculated average functionality of 1.98±.18. The characteristics of Sample D are summarized in Table XI.

TABLE XI

CHARACTERISTICS OF SAMPLES C AND D

<u>Sample</u>	<u>C</u>	<u>D</u>
Notebook Reference	9706-34	9706-38
$\bar{M}_n$ (V. P. O., THF at 37°C)	2225 + 30	2454 + 154
OH Equivalent wt. (Acetylation)	1124 + 15	1240 + 33
Functionality	1.98 ± .05	1.98 ± .18
Ionol Content ^a	545 ppm	180 ppm
Water Content ^b	16 ppm	12 ppm

a) U. V. Spectroscopy

b) Karl Fisher Titration

D. Molecular Weight Distributions of Hydroxy-Telechelic Polyisoprene by Gel Permeation Chromatography

In Part 2, Section C we described the use of Gel Permeation Chromatography (GPC) to determine the molecular weight distribution of 29-EMS-72, a hydroxy-telechelic hydrogenated polyisoprene previously submitted to JPL for evaluation. In the section to follow, we report the use of the same technique to analyze the four hydroxy-telechelic polyisoprenes reported in Sections A and B of this part of the report.

Using the same GPC system discussed in our previous reports, chromatograms were run on Samples A, B, C and D. After correction for baseline drift and normalizing to the same height at the peak maximum, the results shown in Figures 9, 11, 13 and 15 were obtained. These chromatograms were then transformed to integral molecular weight distribution curves using the calibration curve and mathematical methods previously reported, with the results shown in Figures 10, 12, 14 and 16.

Table XII summarizes the numerical results obtained. Note that Sample A, the only product made in a batch type reactor, has a broader molecular weight distribution than the others, all prepared in a continuous reactor. This is best seen in the $\bar{A}_w/\bar{A}_n$ ratio.

In Figure 17 $\bar{M}_n$ is shown plotted against $\bar{A}_n$ for each of the four samples.

Note that with the exception of Sample A, the points lie close to a straight line corresponding to the equation.

$$\bar{M}_n = Q \times \bar{A}_n, \quad \text{Where } Q = 25.7$$

This is to be expected, since the number average molecular weight should correlate linearly with the number average chain length. To the extent that $\bar{A}_n$ actually represents the number average chain length, we may use GPC determined $\bar{A}_n$ values to calculate $\bar{M}_n$, once the constant Q has been determined.

-
7. The accuracy of $\bar{A}_n$ as a measure of the number average chain length is primarily limited by two considerations:
- Constancy of the differential refractometer detector response as the molecular weight of the eluate varies
 - Applicability of the calibration curve of extended chain length versus retention volume determined using polystyrene standard samples of known molecular weight and narrow molecular weight distribution.

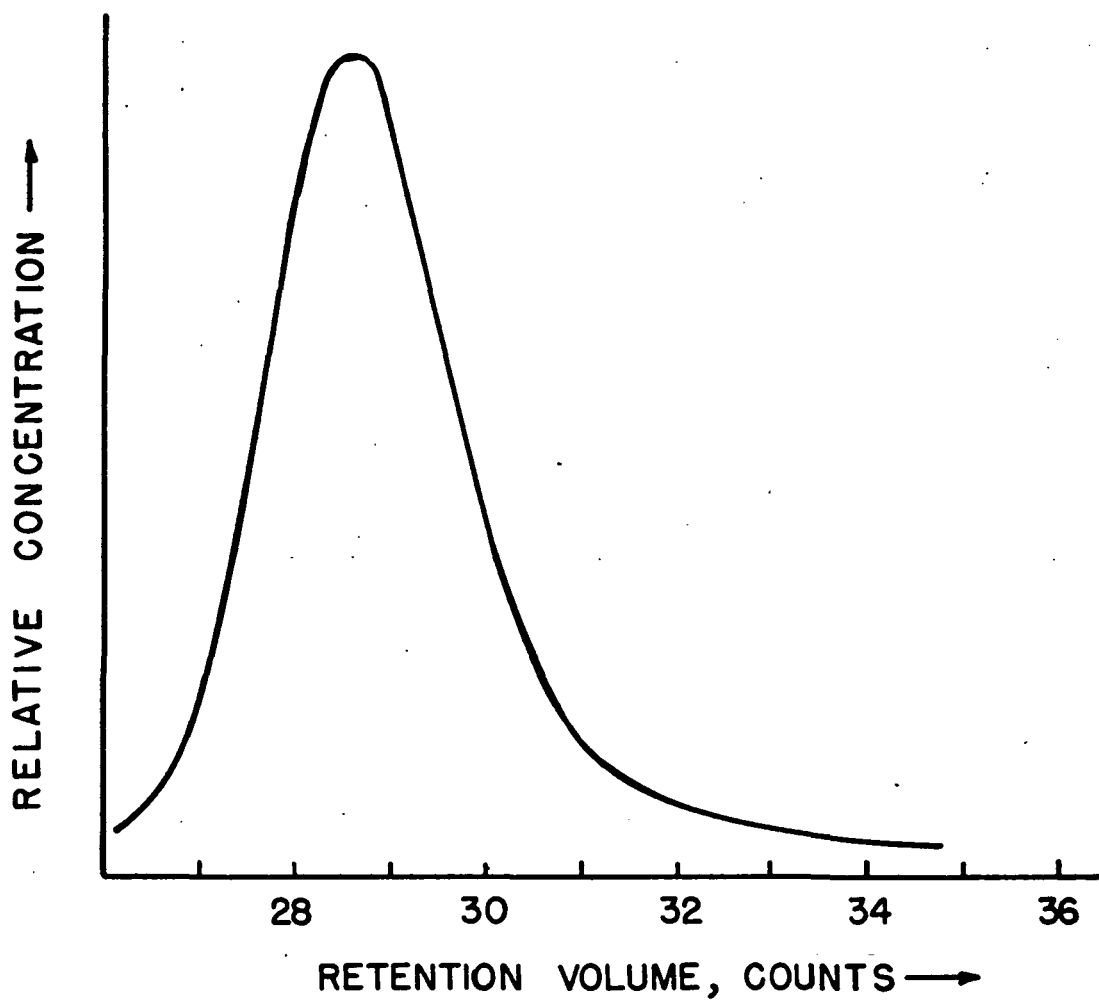


FIG.9. BASELINE - CORRECTED GEL PERMEATION CHROMATOGRAM OF SAMPLE A

FRACTION OF TOTAL POLYMER →

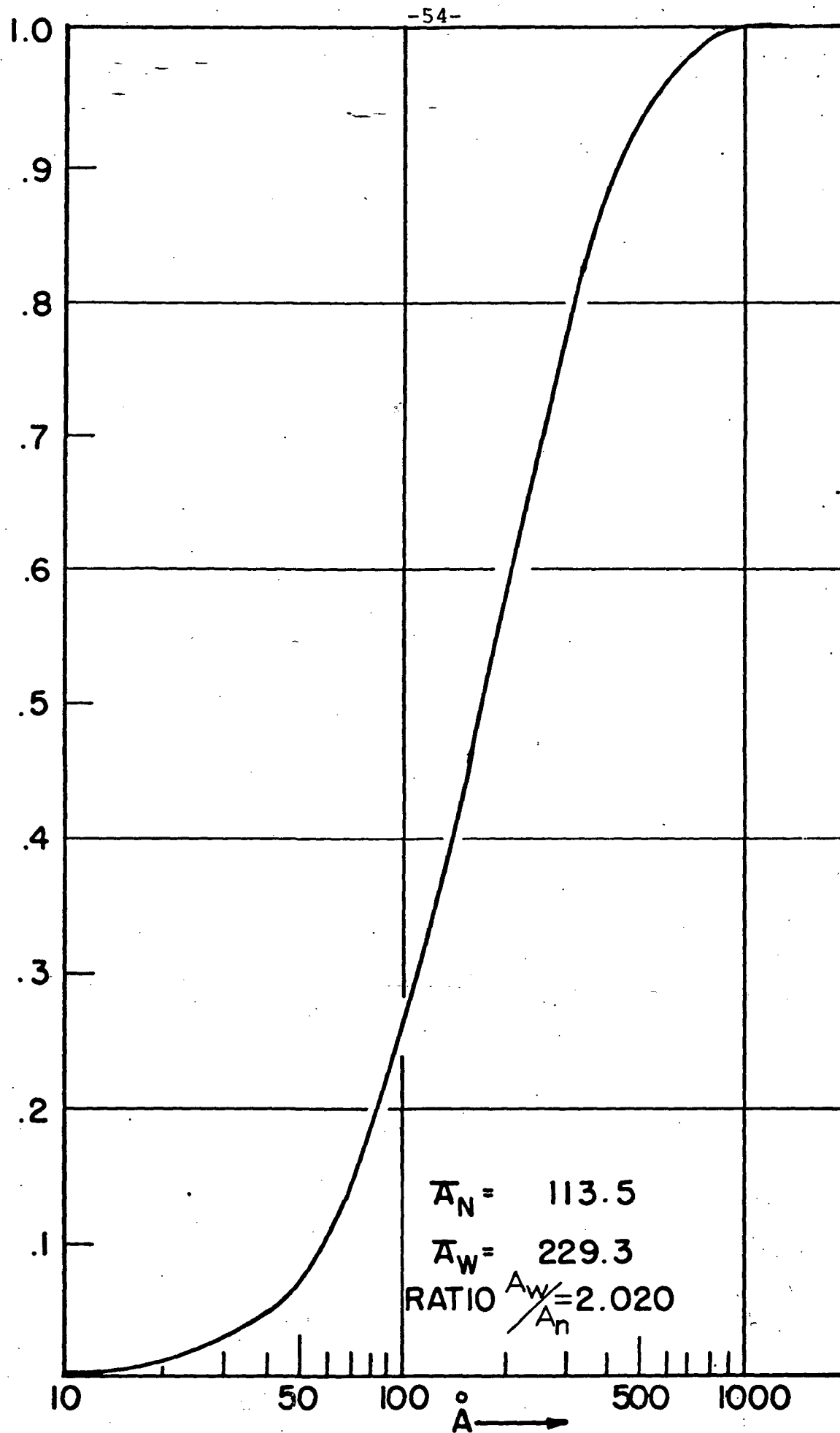


FIG.10. INTEGRAL CHAIN LENGTH DISTRIBUTION, SAMPLE A

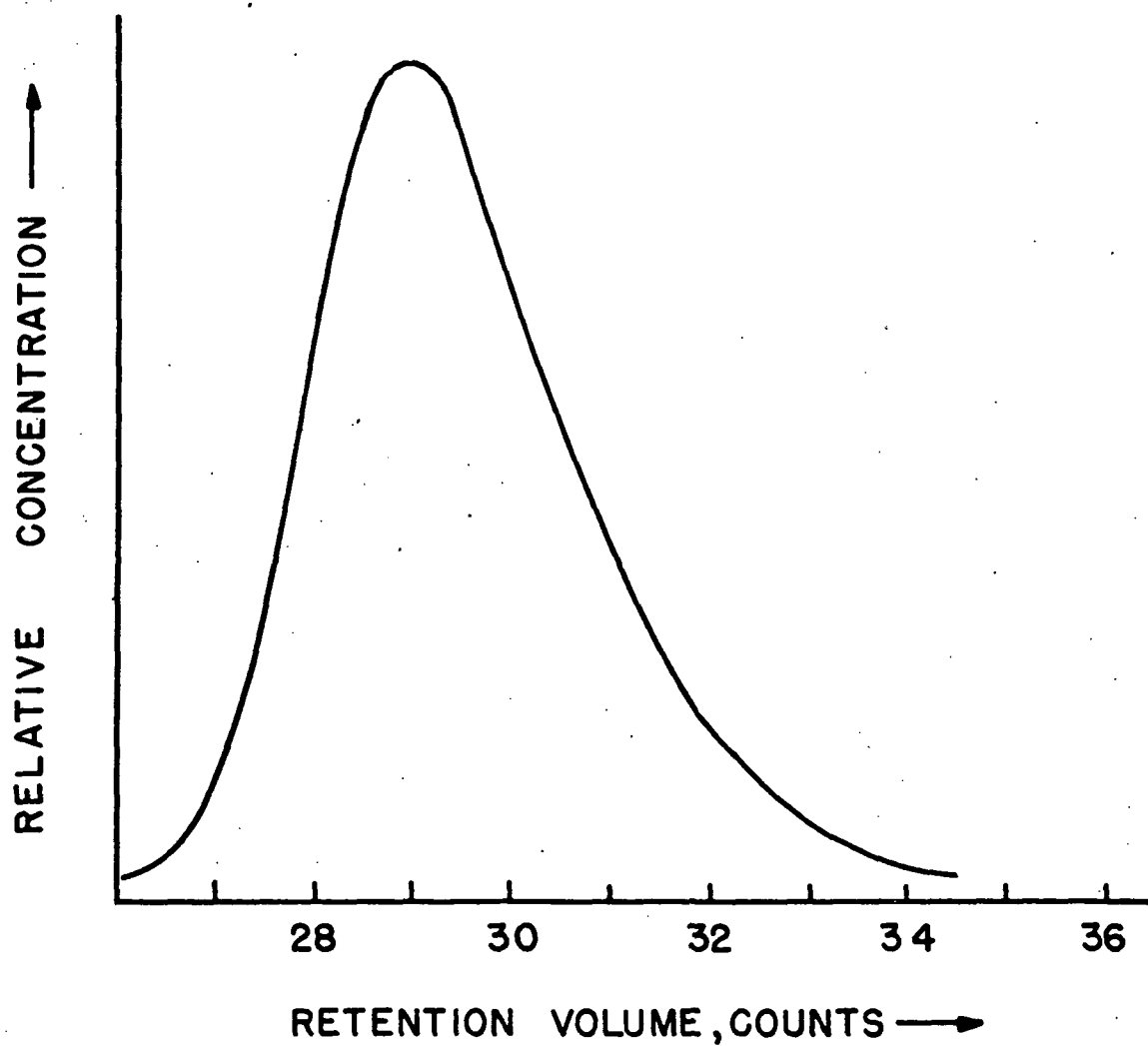


FIG. 11. BASELINE - CORRECTED GEL PERMEATION CHROMATOGRAM OF SAMPLE B

FRACTION OF TOTAL POLYMER →

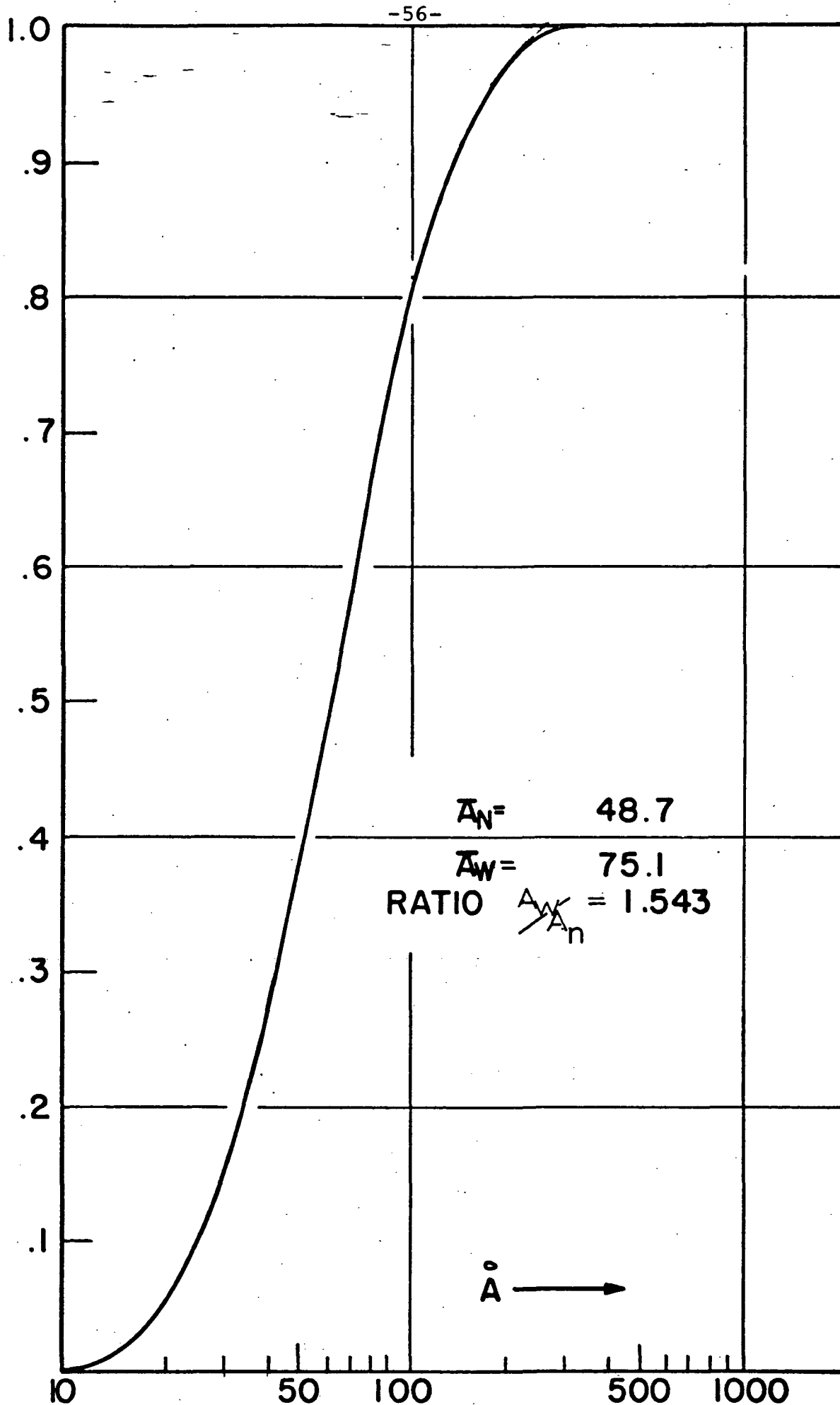


FIG.12. INTEGRAL CHAIN LENGTH DISTRIBUTION, SAMPLE B

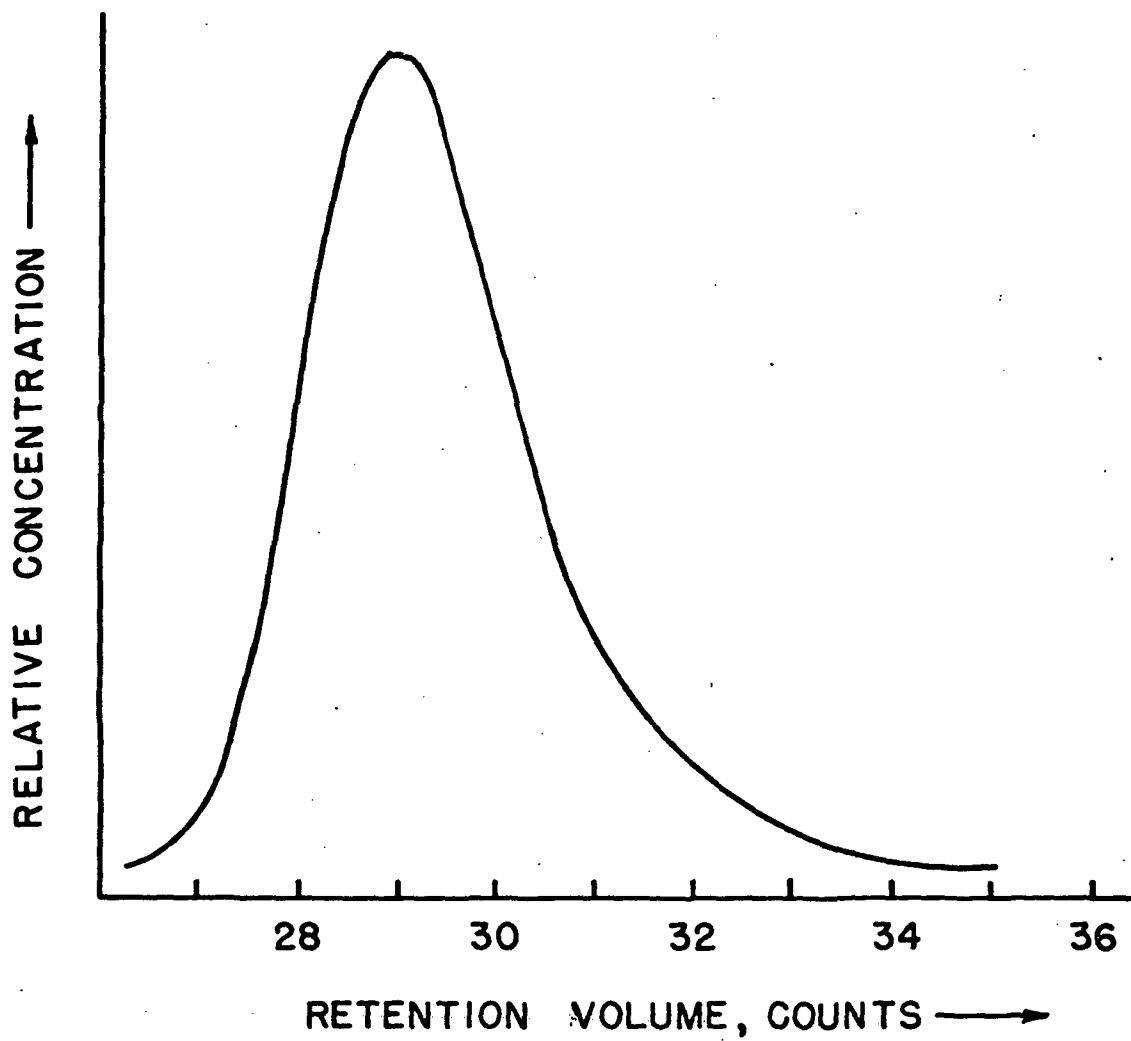


FIG.13. BASELINE - CORRECTED GEL PERMEATION CHROMATOGRAM OF SAMPLE C

FRACTION OF TOTAL POLYMER

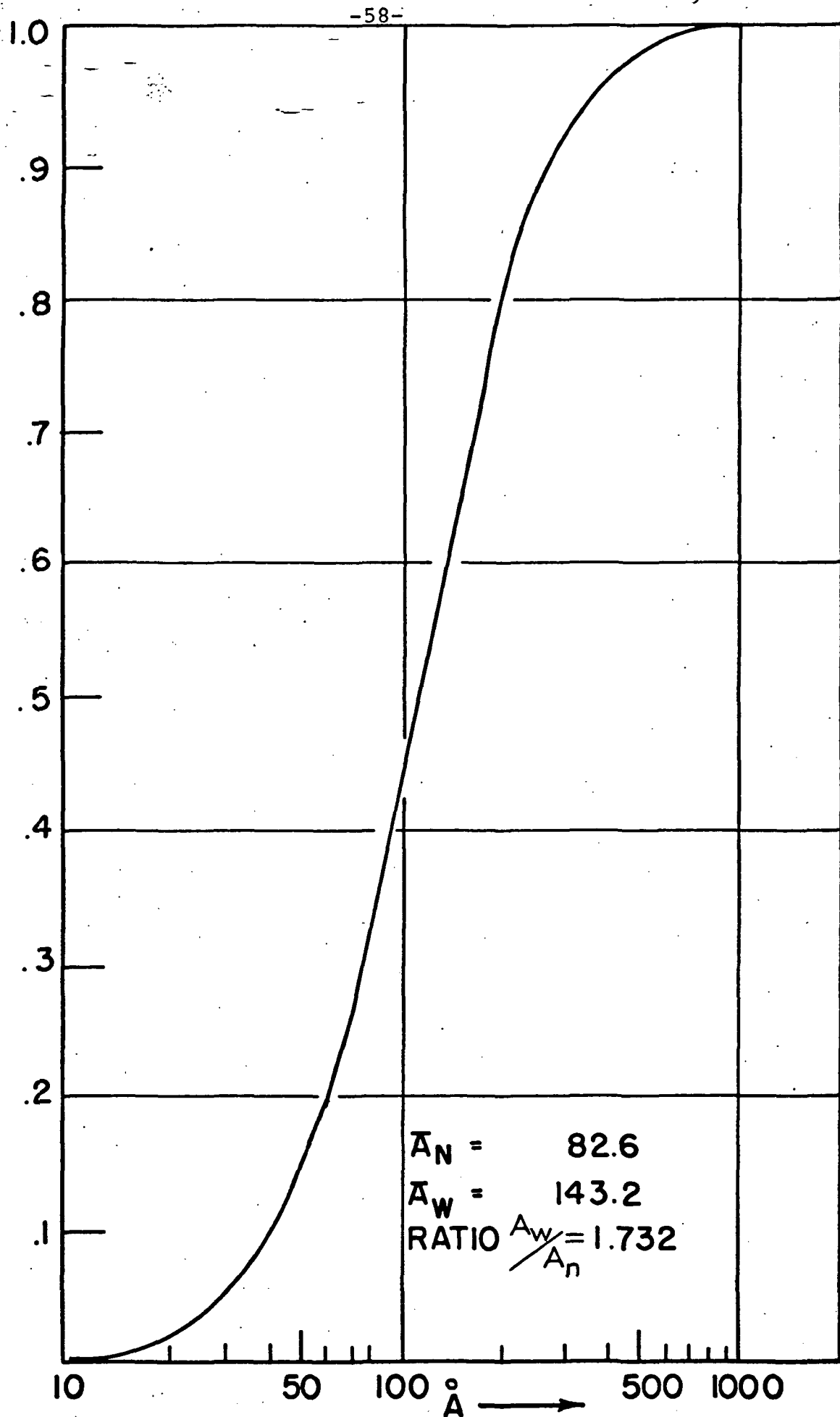


FIG.14. INTEGRAL CHAIN LENGTH DISTRIBUTION, SAMPLE C

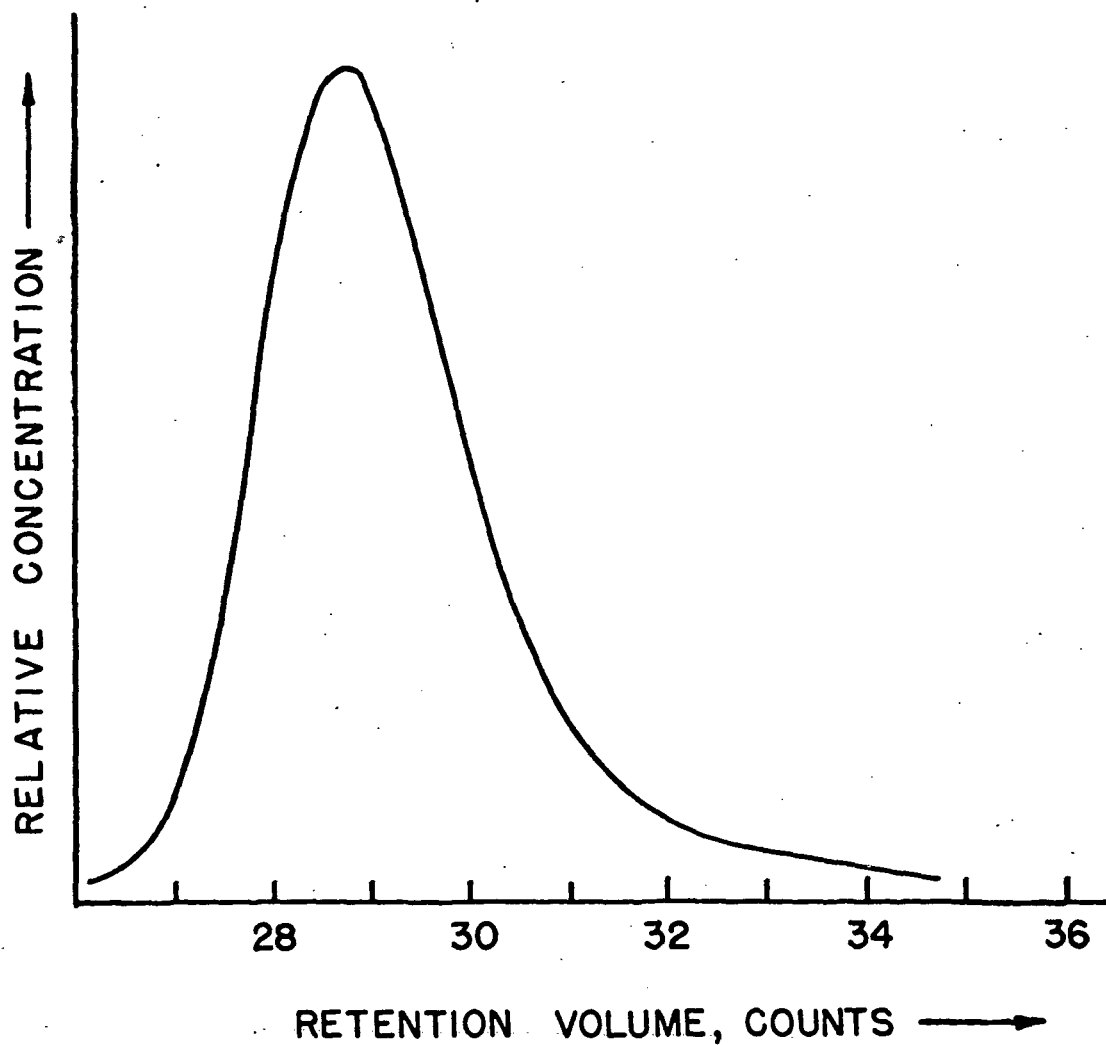


FIG.15. BASELINE - CORRECTED GEL PERMEATION CHROMATOGRAM OF SAMPLE D

FRACTION OF TOTAL POLYMER →

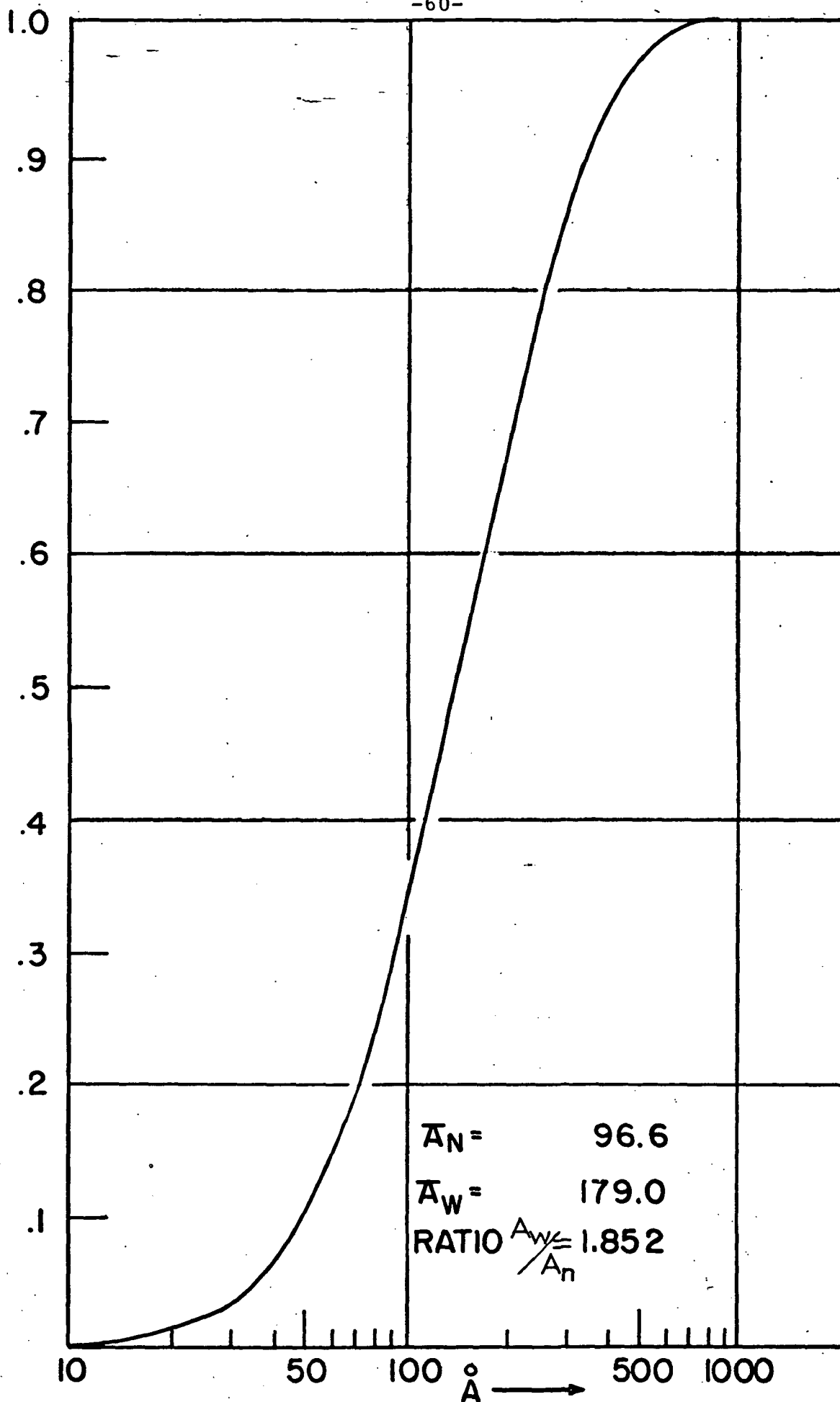


FIG.16. INTEGRAL CHAIN LENGTH DISTRIBUTION, SAMPLE D

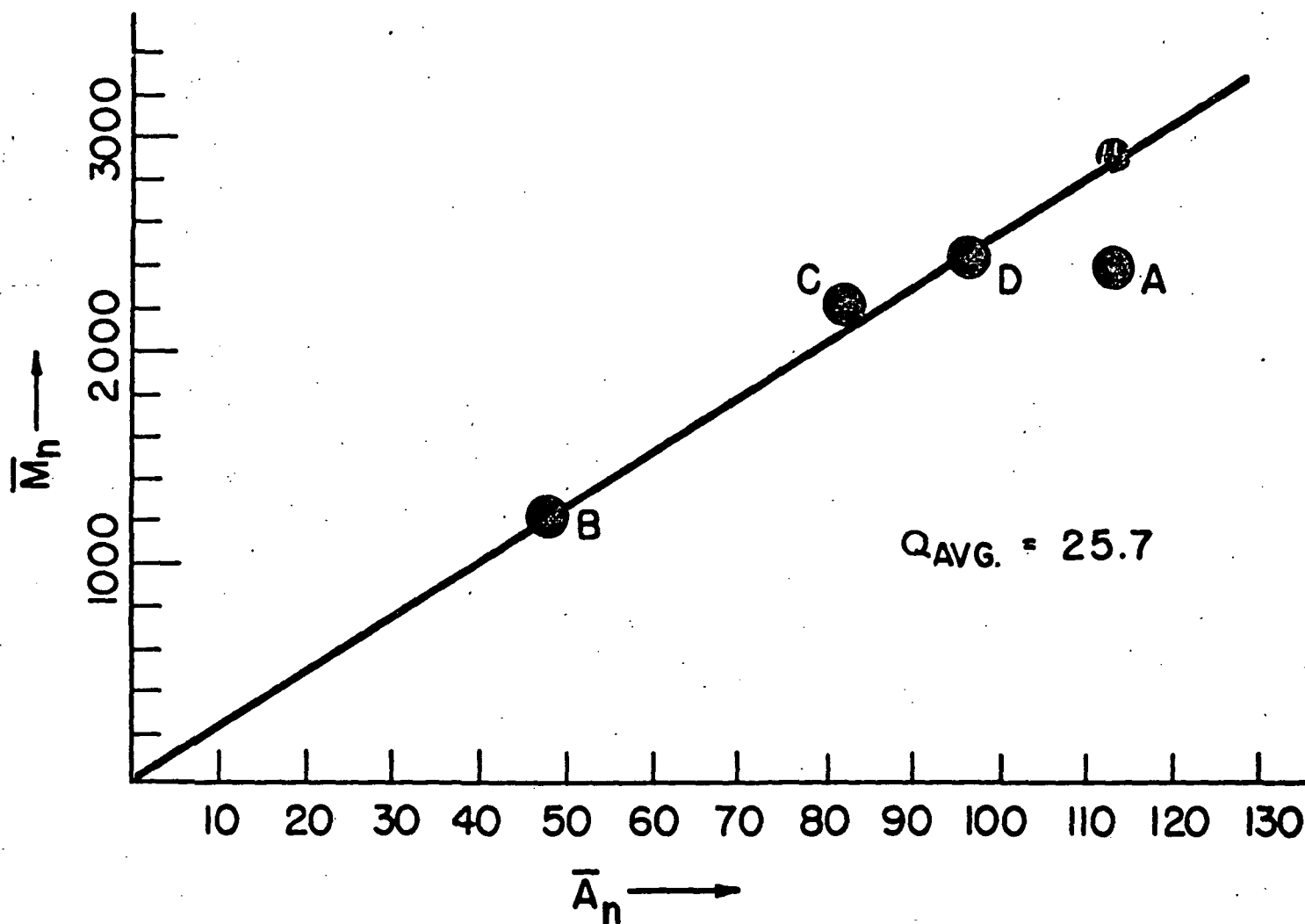


FIG.17.— RELATIONSHIP BETWEEN $\bar{M}_n$ & $\bar{A}_n$ IN HYDROXY-TELECHELIC POLYISOPRENES

TABLE XII
NUMERICAL RESULTS, GPC ANALYSIS OF HYDROXY-TELECHELIC POLYISOPRENE SAMPLES

<u>Sample</u>	$\overline{M}_n^{(a)}$	$\overline{A}_n$	$\overline{A}_w$	$\overline{A}_w/\overline{A}_n$	$Q^{(b)}$
A	2415 ± 177	113.5	229.3	2.02	21.3
B	1230 ± 30	48.7	75.1	1.54	25.3
C	2225 ± 50	82.6	143.2	1.73	26.9
D	2454 ± 154	96.6	179.0	1.85	25.4

a. Vapor Pressure Osmometry

b. $Q = \overline{M}_n/\overline{A}_n$

These results suggest that the VPO determined value of 2415 ± 177 for the M_n of Sample A is in error and that the M_n may actually be closer to 2900. If this is the case, Sample A is higher in functionality than we had previously believed (OH equiv. wt. = 1410 by infrared spectroscopic analysis). Because of this possibility we rechecked the molecular weight determination by VPO. When this was done the result shown in Figure 18 was obtained. With an instrumental calibration factor of 12,800 (determined using pentaerythritol tetrastearate as reference), the intercept of $4.4 \pm .12$ from the V/C vs. C plot gives a value of 2910 ± 80 for the molecular weight of Sample A. This is shown as the half shaded point in Figure 17 and confirms the linear correlation between M_n and A_n . As further evidence accumulates to support this correlation, ^{n} Gel Permeation Chromatography may provide a more dependable source of M_n data which is not subject to the occasional erratic behavior of ^{n} the vapor pressure osmometer.

These results suggest that the prior conclusion (see page 43) that Sample A contained an unresolved monofunctional fraction was in error. The portion of the T.L.C. streak beyond $R_f = .4$ in Fig. 7-A is evidently due to a high mol. wt. difunctional fraction. See Appendix 5, p. 97, for an improved T.L.C. procedure which is useful for broad distribution polymers.

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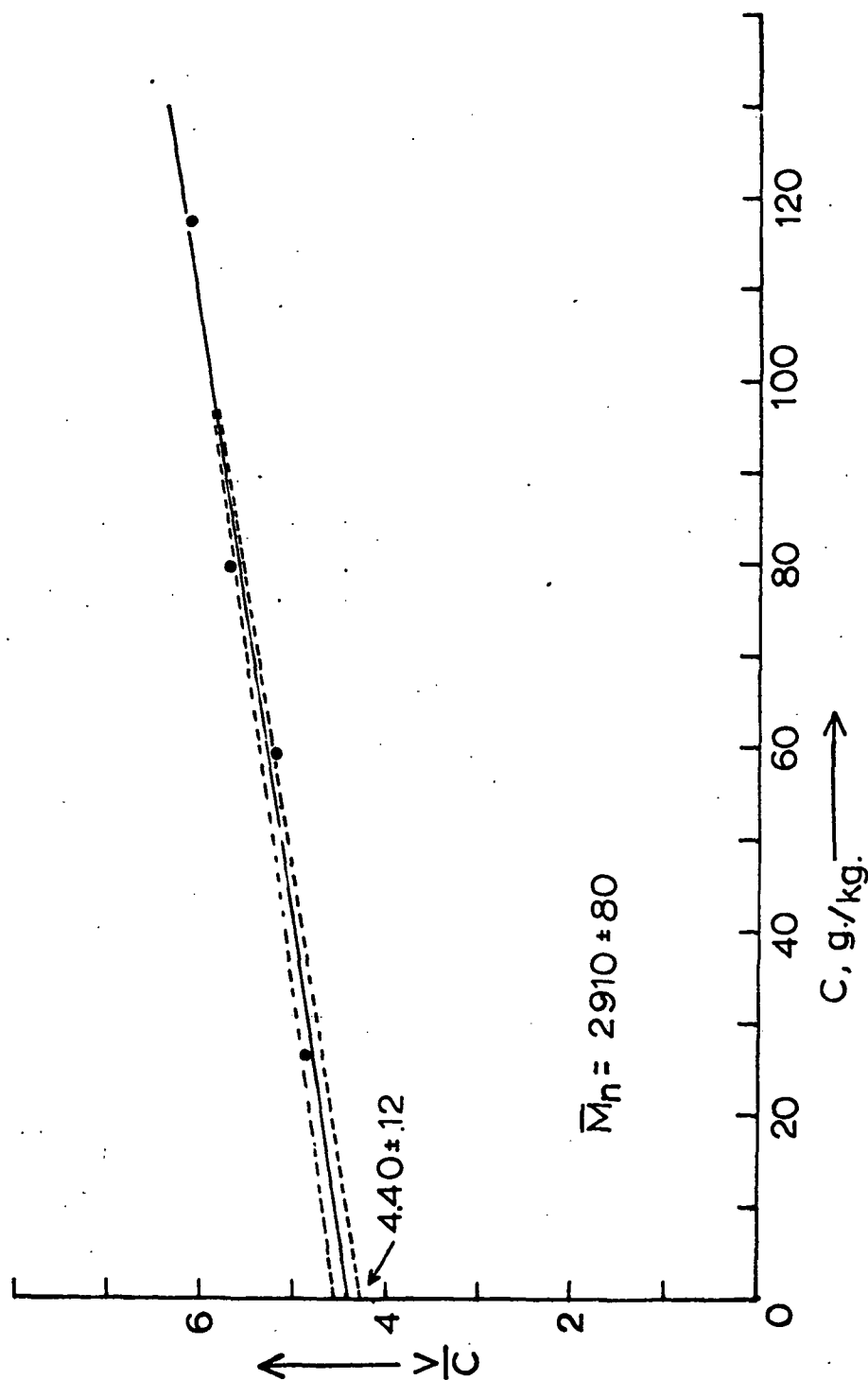


Fig.18. V.P.O. Determination of $\bar{M}_n$, Sample A

E. Preparation of Ester-Telechelic Polyisoprene in the 5-Gallon Stirred Autoclave Reactor

In order to provide J.P.L. with sufficient material to evaluate our hydroxy-telechelic polyisoprene in propellant formulations on a somewhat larger scale, we decided to prepare a one-gallon batch. Our five-gallon batch reactor previously used to prepare the precursor to "Sample A") can be operated with a ten liter charge of isoprene. At the conversions normally obtained between four and six pounds of ester-telechelic polyisoprene can be prepared in a single run. We considered that two such runs would provide an ample supply of starting material for the preparation of the one-gallon sample of hydroxy-telechelic binder prepolymer described above.

1. Polyisoprene Run No. 9769-CAK-2

The parameters for run 9769-CAK-2 are summarized in Table XIII. The isoprene was charged to the five-gallon reactor under a nitrogen atmosphere, the port sealed, and the reactor heated with stirring up to 100°C. This required twenty minutes. At this point a pump was started to feed a 10% solution of diethylazobisisobutyrate in benzene into the reactor at a rate of 8.8 ml./min. Over the 4-3/4 hour run, 2500 ml. (containing 250 gms. DEAB) of the solution was fed in. At the end of this time the heat controller was shut off and cooling water used to rapidly lower the temperature of the reactor to 35°C, at which point the contents was discharged into a receiver through the bottom port. See Figure 19.

The benzene solvent and unpolymerized isoprene were removed by vacuum evaporation to give 2848 grams colorless hazy liquid polymer having a Brookfield viscosity of 64 poise at 25°C.

Examination of the infrared spectrum of the product disclosed some abnormalities in the 1-13 μ region which contains the C-H "wagging" vibrations associated with double bonds. In a "normal" polyisoprene prepared by free radical polymerization under our conditions the ratio of the vinyl (910 cm^{-1}) to vinylidene (890 cm^{-1}) to trisubstituted double bond (840 cm^{-1}) absorbances are in the ratio of .704: .930 = 1.00. However, the spectrum

-
8. Note: the extinction coefficient for the trisubstituted C=C absorption is much lower than that for the vinyl and vinylidene. The product actually contains about 90% cis and trans 1-4 polymerized isoprene.

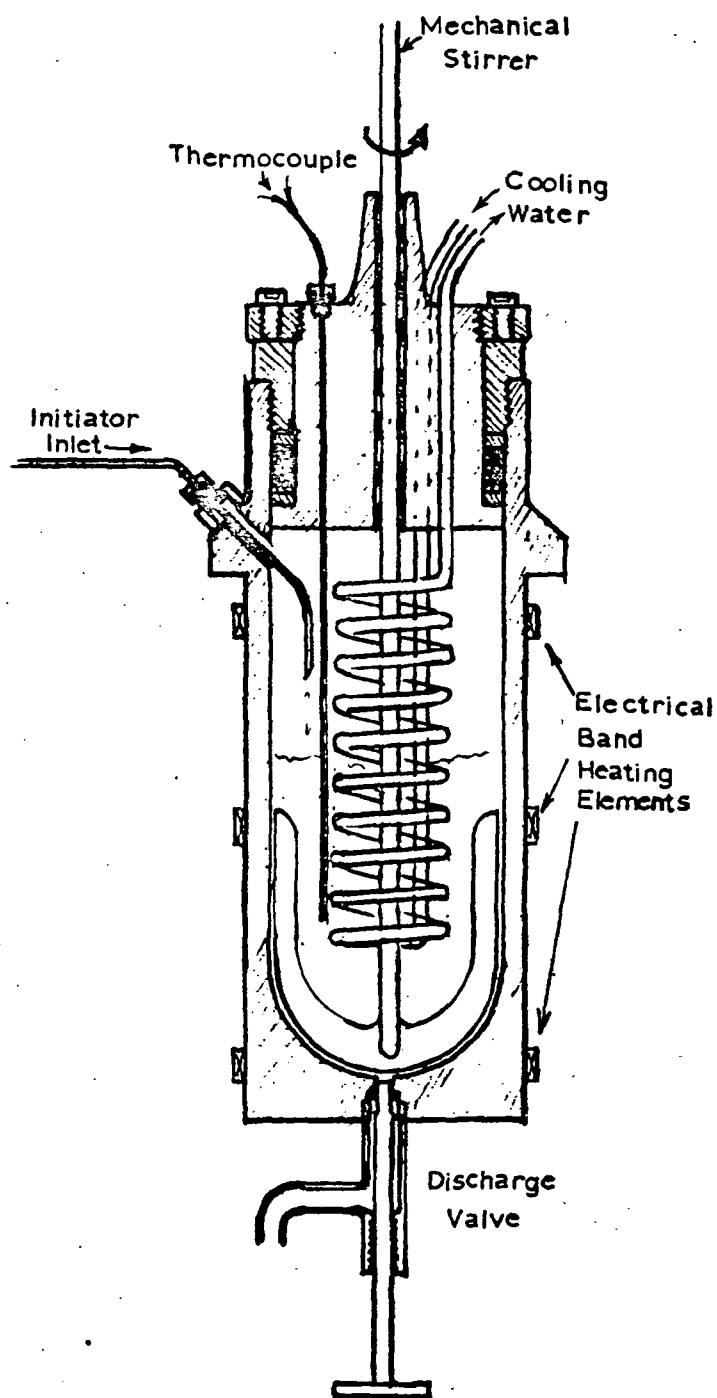


Fig.19 5-Gallon Stirred Autoclave Reactor

TABLE XIII

POLYISOPRENE RUN NO. 9769-2

Charged to Reactor Initially

Isoprene	6860 grams
----------	------------

Fed During Run

DEAB	250 grams
Benzene	1980 grams

Reaction Conditions

Temperature	99-101°C
Pressure	83-110 psi
Time	4 hours 45 minutes

Productivity

Yield	2848 grams
Conversion	41.2%
Conversion Rate	8.67% per hour

of the product from run 9769-CAK-2 exhibited these absorbances in the ratio of $1.03 = 1.69:1.00$, showing a significant enhancement of the 1-2 and 3-4 content as measured by the vinylidene and vinyl absorbances⁹.

The number average molecular weight of the product from run 9769-CAK-2 was determined by vapor pressure osmometry in toluene at 37°C and found to be 2700 ± 100 . Infrared spectroscopy using ethyl pivalate as a reference standard gave a value of 2150 for the ester equivalent weight. This implies an average functionality of 1.26 ester groups per molecule.

To verify this unexpected result, a small quantity of the product was subjected to lithium aluminum hydride reduction. A solution of 36.5 g. 9769-CAK-2 in 100 ml. abs. ether was added dropwise with stirring to a suspension of 2.1 grams lithium aluminum hydride in 150 ml. abs. ether. After refluxing the mixture for one hour, the excess hydride was decomposed by adding successively 2.1 ml. water, 2.1 ml. 15% NaOH solution and 6.3 ml. water. The clear supernatant ether layer was then decanted, filtered and evaporated to give 28.7 grams colorless oil, showing no ester absorbance in the infrared.

Determination of the hydroxyl equivalent weight by infrared spectroscopy (25% ethyl acetate in CCl_4 used as solvent, reopentyl alcohol used as reference compound) gave the value 2180 g. per equivalent of hydroxyl, quite close to the value 2150 obtained on the ester terminated precursor.

Thin layer chromatography of the hydride reduced product using CH_2Cl_2 as the developing solvent gave a chromatogram showing an elongated streak stretching from the origin of the plate clear up to the solvent front. Under these conditions a difunctional polyisoprene of 2700 molecular weight should show little or no material past $R_f = 0.6$ on the TLC plate.

-
9. This effect is similar to the result noted in a previous experiment, run 8908-CAK-133, in which no DEAB initiator was used at all. The product from this run, the so-called "Thermal-Polyisoprene", was obtained in very low yield (~ 700) non-functional polymer. The infrared spectrum showed vinyl to vinylidene to trisubstituted $\text{C}=\text{C}$ absorbances in the ratio of $1.31:2.35:1.00$.

Two dimensional thin layer chromatography using 2½% ethanol/heptane in the first development, and using acetone in the second development at right angles to the first* gave the interesting result that the polymer contained no monofunctional fraction. The main components were difunctional and non-functional. In addition, the difunctional component showed chromatographic behavior indicative of a very broad molecular weight distribution.

2. Examination of Possible Factors in the Low Functionality Attained in Run 9769-CAK-2

Since none of our previous isoprene polymerizations had yielded products having functionalities appreciably below two, the low ester functionality (1.26 ± 0.04) measured for the product of run 9769-CAK-2 was interpreted to indicate that something out of the ordinary occurred during the polymerization, either in the way the polymerization was run or in the purity of one of the starting materials. Accordingly we examined each possibility in detail.

a. Monomer Purity

The isoprene used in polymerization run 9769-CAK-2 was Matheson Coleman and Bell, Practical Grade, which had been distilled at atmospheric pressure under nitrogen through a 40" long, 1½" diameter, 32 plate Oldershaw distillation column operated at 100% takeoff. A typical distillation curve is shown in Figure 11.

Gas chromatographic analysis¹⁰ of the fraction distilling over the range 33-35°C gave the result shown in Figure 21, compared with a similar chromatogram of the starting material in Figure 22. The major impurity in the practical grade isoprene was found to be a higher boiling substance, probably dimeric in nature. Its retention time of 14.2 minutes corresponds to one of the major components in commercial "dipentene" and is probably *dl*-limonene or a closely related structure. The distillation reduced this component from 5.98% to 0.05%. Two other components of unknown nature were found at 4.7 minutes (0.05%) and 6.8 minutes (0.25%). The largest impurity in the distilled isoprene was also in the starting material. It had a retention time of 1.1 minute and comprised 0.49% of the starting material and 0.55% of the distilled

*A detailed description of the method will be given in Appendix 5 following this section.

10. A Perkin-Elmer Model 990 with hydrogen flame ionization detector coupled to an Infotronics logarithmic attenuator and electronic integrator was used for the analyses. A 200 cm x 1/8" column of 10% Carbowax 20M on 40/60 Chromosorb T operating at a flow rate of 25cc/min. gave the required chromatographic separation. The following program was used. Inject 0.2µl of sample, operate isothermally for 4 min. at 60°C, program to 175°C at 8°/min., remain at 175°C for duration of chromatogram.

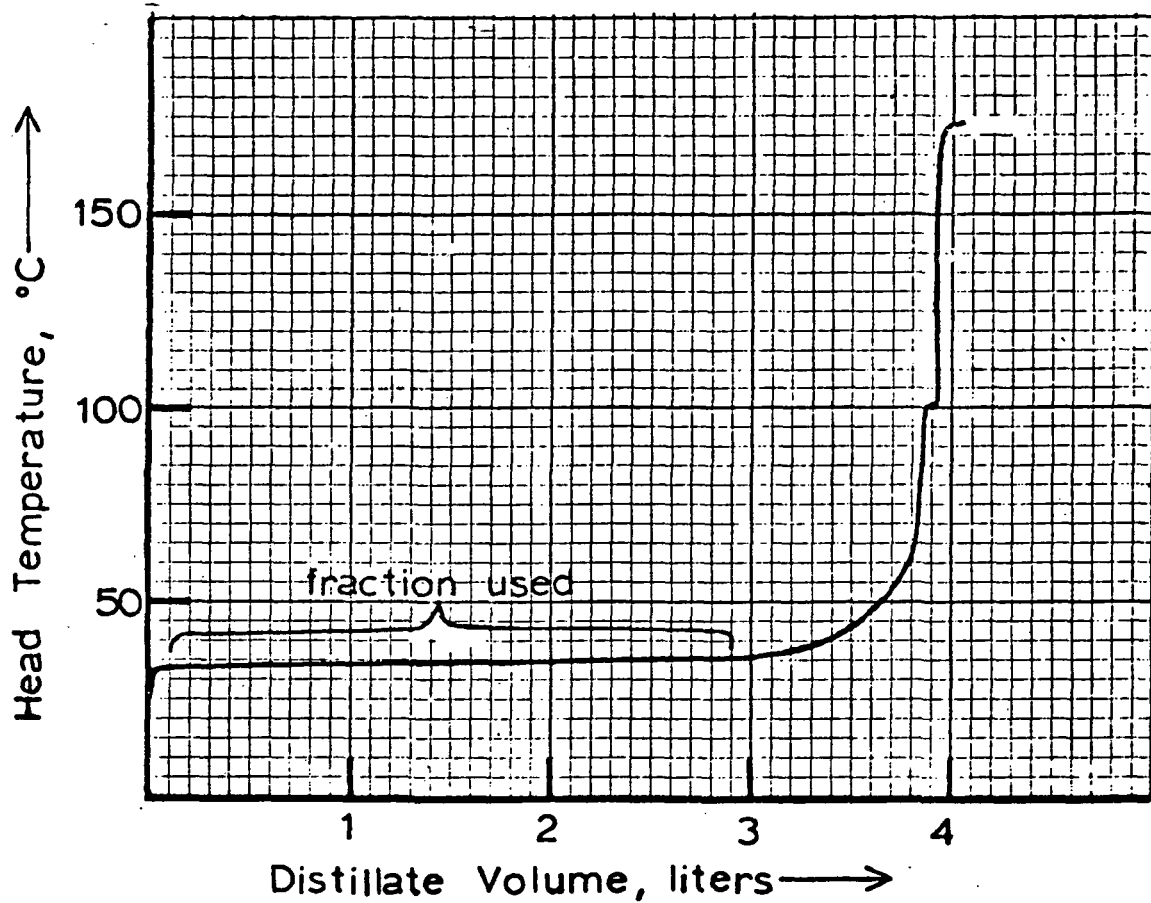


Fig.20. Isoprene Distillation Curve

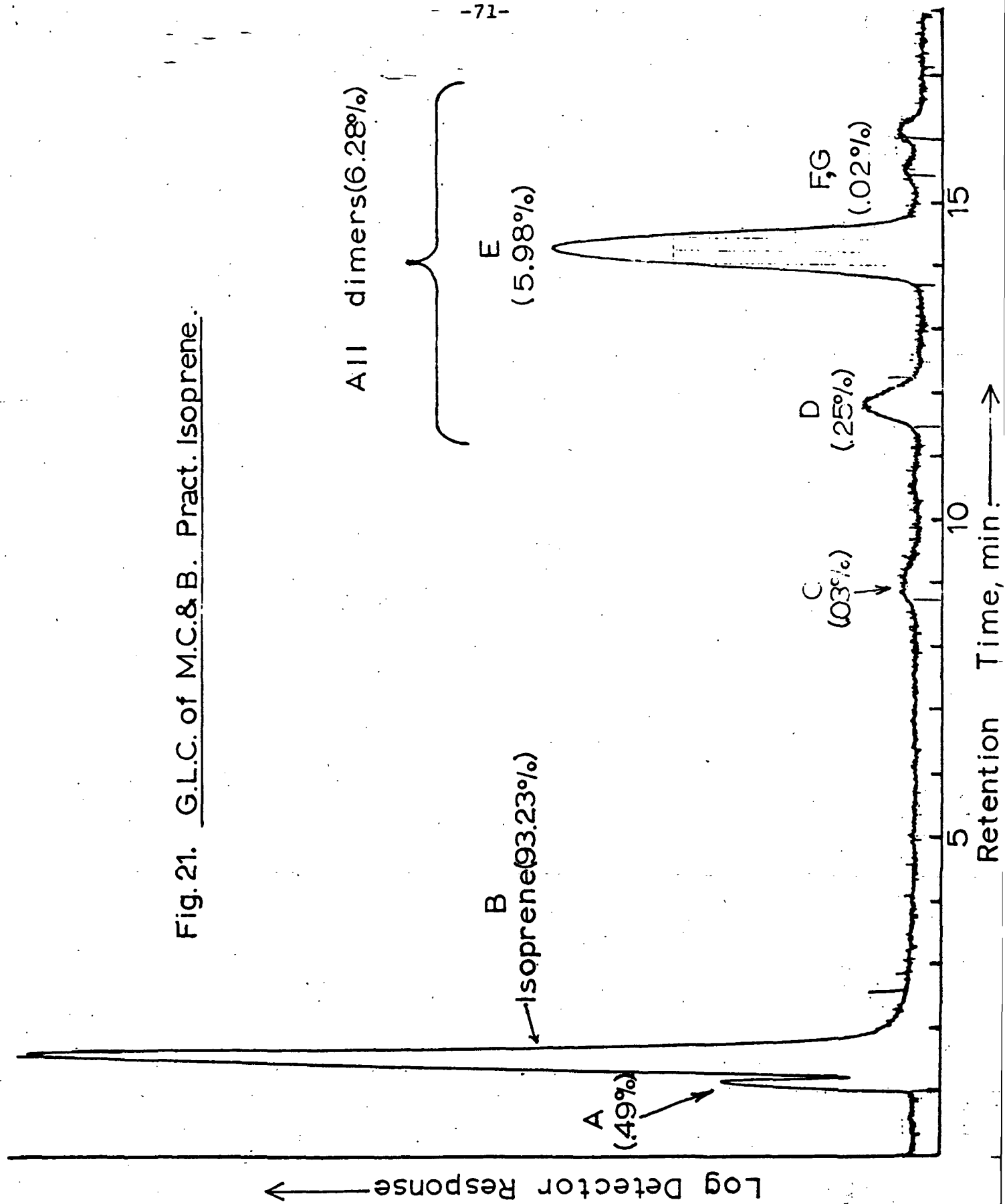
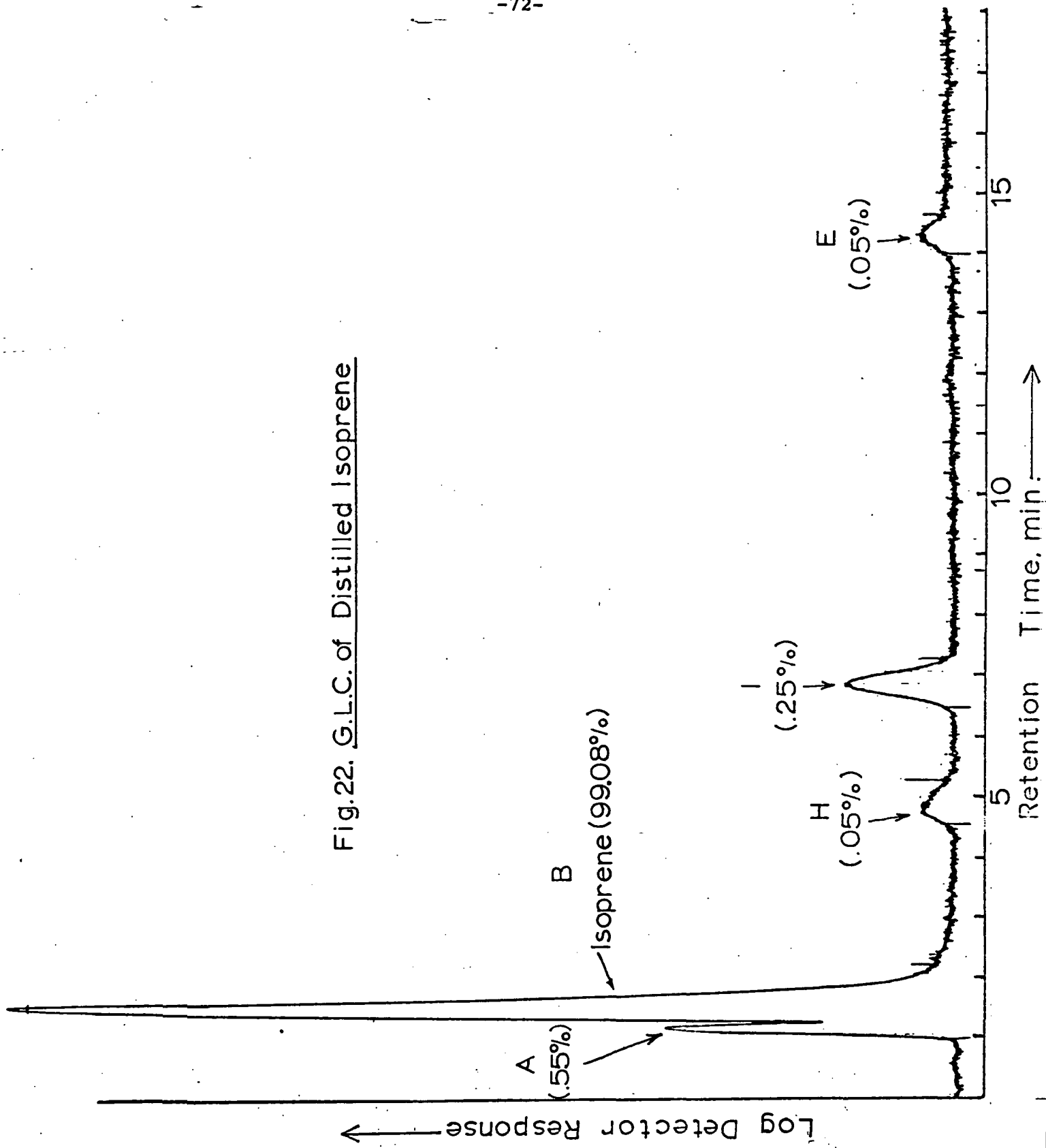


Fig. 21. G.L.C. of M.C.&B. Pract. Isoprene.

Fig.22. G.L.C. of Distilled Isoprene



product. Isoprene comprised 93.23% of the practical grade isoprene and 99.08% of the distilled material used in the polymerization.

When the distillation was run using a reflux ratio of 9:1 (10% takeoff, 90% return to column) it was found that the components of longer retention time than isoprene (C, D, E, F, G, H and I of Figures 12 and 13) could all be eliminated entirely; however, the short retention time component (A) was too close to isoprene in boiling point to be completely separated by distillation. The isoprene obtained in this way was 99.7% purity containing 0.3% of the unknown component "A".

When the mass spectrograph was used in conjunction with the gas chromatograph, component A was identified as pentene-2 by its molecular ion at $m/e=70$ and by its characteristic fragmentation pattern.

In summary, the isoprene used in run 9769-CAK-2 was 99.08% pure and contained 0.05% dimer, 0.55% pentene-2 and 0.30% of two unknown components. A more careful distillation in which a higher reflux ratio was used gave 99.7% pure isoprene containing 0.3% pentene-2 as the sole impurity which should have no effect upon the polymerization..

b. Initiator Purity

The DEAB used in polymerization 9769-CAK-2 had been prepared March 10, 1969, by treatment of azobisisobutyronitrile with ethanolic HCl and hydrolysis of the resulting iminoether hydrochloride to yield the ester. For details of the preparation see p. 41-42 in our triennial report. Between the preparation in March of 1969 and its use in run 9769-CAK-2 in February of 1971, the DEAB had been stored in a polyethylene carboy, tightly stoppered and placed in a cold room at 0°C.

A sample of the remaining DEAB was taken and analyzed to determine whether deterioration had occurred during the 1 year 11 month storage at 0°C. Melting point analysis showed that the sample was impure--melting commenced at -21°C and was complete at -11°C. A freshly prepared sample of DEAB melts at -10 to -5°C. Comparison of the infrared spectra showed only minor differences, however, chiefly in weak shoulders on major peaks in the spectrum of the DEAB used in run 9247-CAK-2. These weak absorbances were at 1620-1660 cm^{-1} and 940-980 cm^{-1} .

c. Initiator Feed to the Reactor

When the initiator solution feed schedule from run 9769-CAK-2 was examined in detail it was noted that the pumping rate of the Lapp-Diaphragm pump was not constant and required manual correction. Figure 23 shows the rate profile for this run. The dashed line is the desired rate.

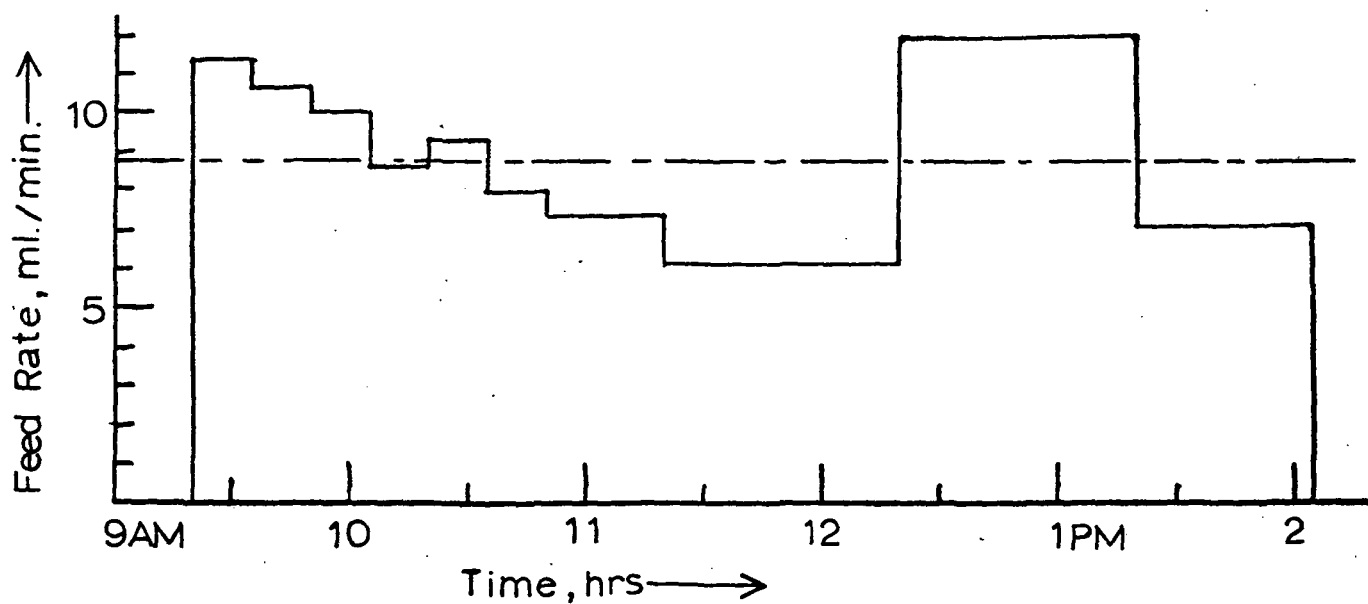
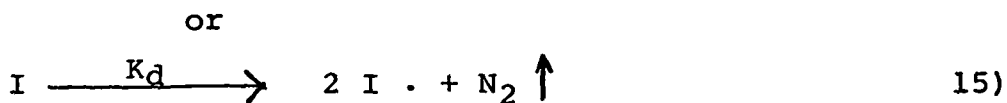
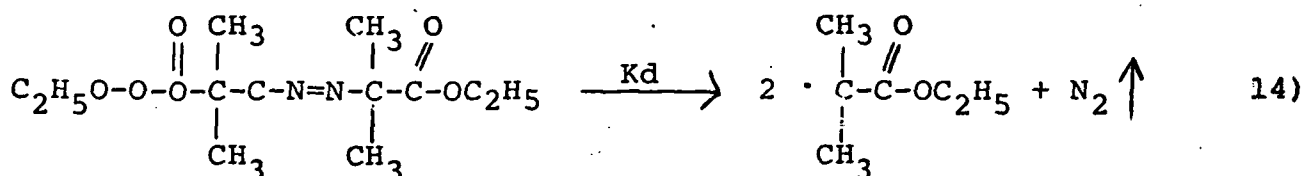


Fig.23. Initiator Feed Rate Profile, Run 9769-CAK-2

The consequences of a variable feed rate of initiator are as follows. DEAB decomposes by the reaction below which follows first order kinetics:



Where: $\frac{d[I]}{dt} = -K_d [I]$ K_d is the first order rate constant in units of min.^{-1} . (16)

At the same time that the initiator is being destroyed by decomposition to initiator radicals, it is being replenished by the initiator feed into the reactor. This effect upon the initiator concentration is given by:

$$\frac{d[I]}{dt} = K_f \quad (17)$$

Where: K_f is the feed rate in $\frac{\text{moles}}{\text{liter-min.}}$

The competition between these two processes gives a steady state initiator concentration which is the solution to the differential equation:

$$\frac{d[I]}{dt} = K_f - K_d [I] \quad (18)$$

For the situation in which termination is by recombination of polymer radicals alone, Flory¹¹ has derived the relationship between the number average degree of polymerization, $\bar{X}_n$, and the relative concentrations of initiator and monomer:

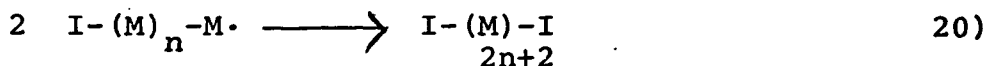
$$\bar{X}_n = \frac{K_p}{(fK_dK_t)^{1/2}} \frac{[M]}{[I]^{1/2}} = C \frac{[M]}{[I]^{1/2}} \quad (19)$$

Where: K_p is the rate of propagation, K_d is the rate of dissociation of initiator and K_t is the rate of recombination of polymer radicals.

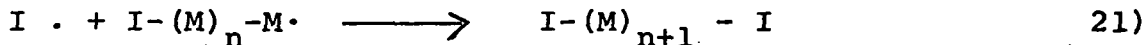
However, in the derivation of the above equation it was assumed that the only termination reaction involved the inter-

11. Paul J. Flory, Principles of Polymer Chemistry, p. 133.

action of two propagative, polymer chain radicals:



In systems where the initiator radical concentration is high enough, another termination reaction becomes possible. This involves one initiator radical and one polymer chain radical and, in the case of diene monomers, also results in a difunctional coupled product:



When the above reaction is considered the only mode of termination one obtains a different relationship between the degree of polymerization and the initiator concentration:

$$\bar{X}_n = \frac{k_p k_i}{k_d k_t} \frac{[\text{M}]^2}{[\text{I}]} = c' \frac{[\text{M}]^2}{[\text{I}]} = c' \left(\frac{[\text{M}]}{\sqrt{[\text{I}]}} \right)^2 \quad (22)$$

We thus see that in order to produce a uniform product with as narrow a molecular weight distribution as possible, the ratio between the monomer concentration and the square root of the initiator concentration must be maintained constant in either case, with the true dependance of the degree of polymerization on this ratio being somewhere in between:

$$\bar{X}_n \approx c'' \left[\frac{[\text{M}]}{\sqrt{[\text{I}]}} \right]^a, \quad 1 \leq a \leq 2 \quad (23)$$

Where the value of a depends upon the relative importance of 20) and 21).

What is the effect of an irregular initiator feed rate profile, such as shown in Figure 23, upon the initiator concentration? To answer this question, an analog computer simulation program¹² was used to provide a model of the polymerization reactor, initiator feed system, and initiator decomposition kinetics. The model allows for an initial programmed heating of the reactor with calculation of the rate of decomposition of the initiator at different temperatures using the Arrhenius equation. In addition, a variable feed rate can be programmed. To simplify the present task, no further chemistry past the point of initiator decomposition was simulated in this model.

The results of an analog simulation of a hypothetical polymerization run are shown in Figure 24. The solid curve gives the feed rate assumed for the run in units of 100 ml. per hour. This feed schedule was chosen so as to exceed the variations normally encountered in our actual polymerizations. In this

12. IBM Continuous System Modeling Program, 1130-CX-13X, described in detail in Appendix 4 following this section.

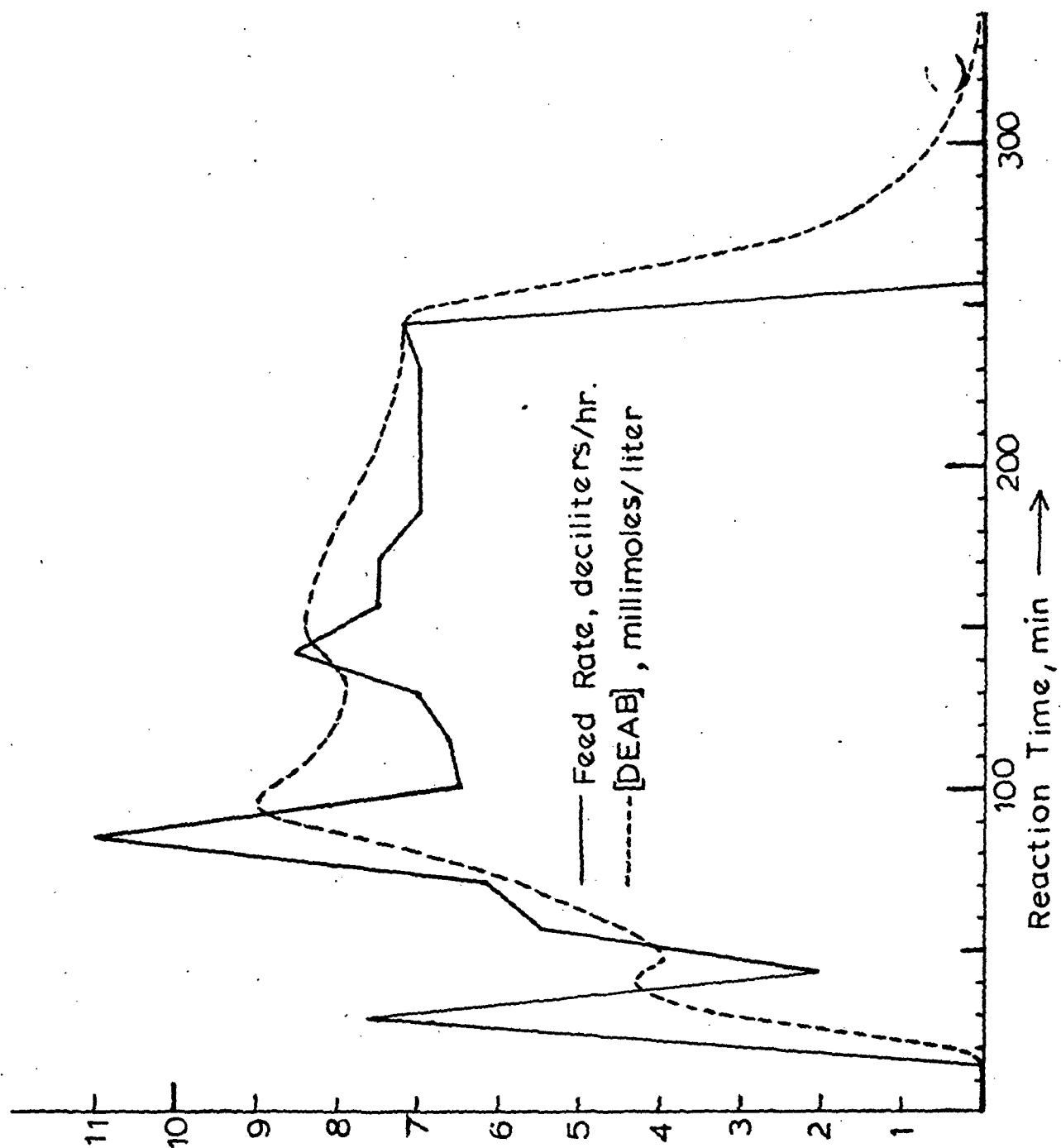


Fig.24. Initiator Concentration vs Feed Rate

simulated run, initiator feed commenced at $t=15$ min., rapidly rose to about 750 ml./hr., decreased to 200ml./hr., increased to a peak of 1100 ml./hr. and finally stabilized near 700 ml./hr. until the pumping was decreased to zero at the end of the run. The DEAB concentration followed the feed rate, however, it tended to lag behind and showed smoother variations than the feed rate. The quantity D, defined as the reciprocal of the square root of the DEAB concentration, shows an even smaller variation with initiator feed rate. This is shown in Figure 25. Since the quantity D is directly proportional to the degree of polymerization, it is the value of D which is relevant to the molecular weight of the polyisoprene produced at a given point during the run. Thus from $t=80$ min. to $t=250$ min. the average molecular weight should vary in proportion to the extremes in the value of D, namely 11 to 13 ($\pm 8\%$ from the mean), rather than in proportion to the extremes in feed rate which varied from 650 to 1100 ml./hr. ($\pm 26\%$ from the mean).

Figure 25 does, however, illustrate the large effect of the low DEAB concentration which was present at the startup of the hypothetical run as well as the effect of stopping feeding the initiator at the end of the run. In our actual polymerization run #9769-CAK-2, the former situation applies since no DEAB was present in the reactor at the beginning of the run. However, the latter situation does not apply since the reactor was cooled and the run terminated at the same time that the feed pump was shut off.

As a result of these studies of the monomer purity, initiator purity and initiator feed rate schedule encountered in run 9769-CAK-2 it was concluded that room for improvement existed in each of the areas examined, but that the most probable cause of the low functionality was related to the non-uniformities of pumping the initiator into the reactor.

It was decided that the following improvements would be put into effect in subsequent isoprene polymerizations:

- a. Modify the initiator feed system to allow a more uniform feed rate.
- b. Optimize the feed rate and initial DEAB concentration to avoid the low DEAB level noted in the beginning of the run in Figure 24.
- c. Use freshly prepared DEAB.
- d. Use a higher reflux ratio in the isoprene distillation to minimize dimer content.

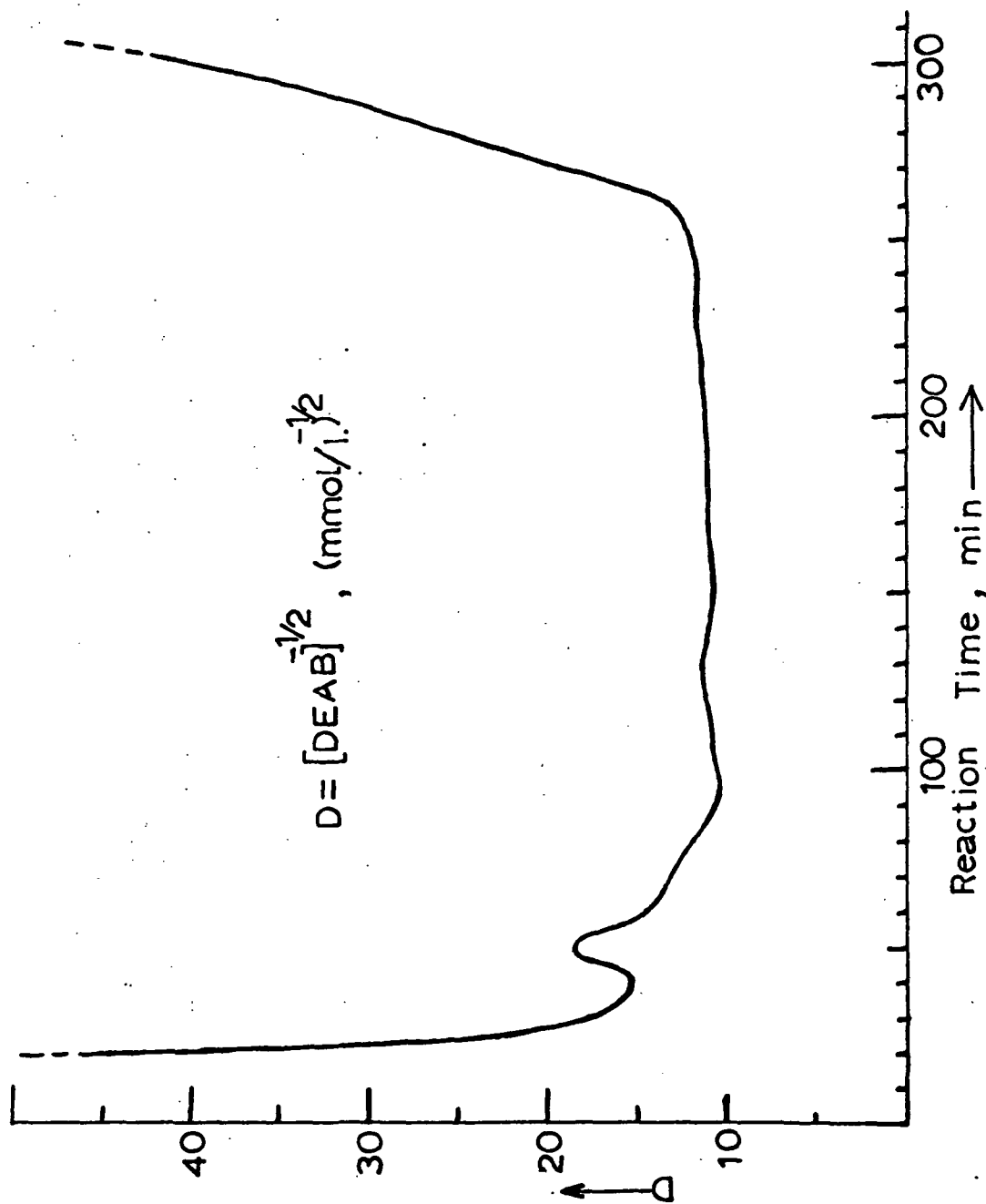


Fig.25. Effect of Pump Fluctuations

3. Implementation of Process Improvements

a. Change Initiator Feed Pump

The balky pump responsible for the erratic initiator feed rate profile shown in Figure 23 was replaced with a chemical proportioning pump of the constant rate positive piston displacement type¹³. In this pump a cylinder containing the entire charge of initiator is traversed by a piston driven by an 8-pitch screw powered by a constant rate mechanical drive. The single stroke discharges the 800 ml. contents of the cylinder at a rate which can be set over the range from 0.1 to 12.2 ml. per minute. This allows run times from a little over an hour at the fastest rates to several days at the slower rates.

Since the maximum feed volume is limited in the new pump, we decided to change the DEAB concentration in the feed solution from 10% to 50%.

b. Feed Rate Optimization Using Analog Simulation

The IBM continuous systems modelling program (CSMP) referred to in section 2-C was used to simulate an analog computer model of the initiator feed system and DEAB decomposition kinetics. This simulation enabled us to determine optimum initial DEAB concentrations as well as feed rate schedules to give a uniform DEAB concentration for the duration of a batch polymerization in the 5-gallon autoclave.

To facilitate the actual use of the results in polymerization runs, a constant rate of feed was selected, commencing when the reactor temperature (determined by a realistic initial heating profile) reached a preselected point. It was found that starting the DEAB feed at a temperature below 80°C resulted in an initial peak in DEAB concentration. This resulted from the low decomposition rate of DEAB at temperatures below 80°C. Conversely, waiting until the reaction temperature had reached the operating temperature of 100°C resulted in an initiator starved condition early in the run. This was caused by the decomposition of the initially charged DEAB before feed was started. A good compromise was achieved when the feed was started at 90°C. Figure 26 illustrates this effect for pumping a 10% solution of DEAB into a 10 liter initial volume at a rate of 500 ml./hr. In these simulated runs the initial DEAB concentration $DEAB_0$ was set at 0.005 M. Note that after 80 minutes pumping all three runs converged to the same initiator level.

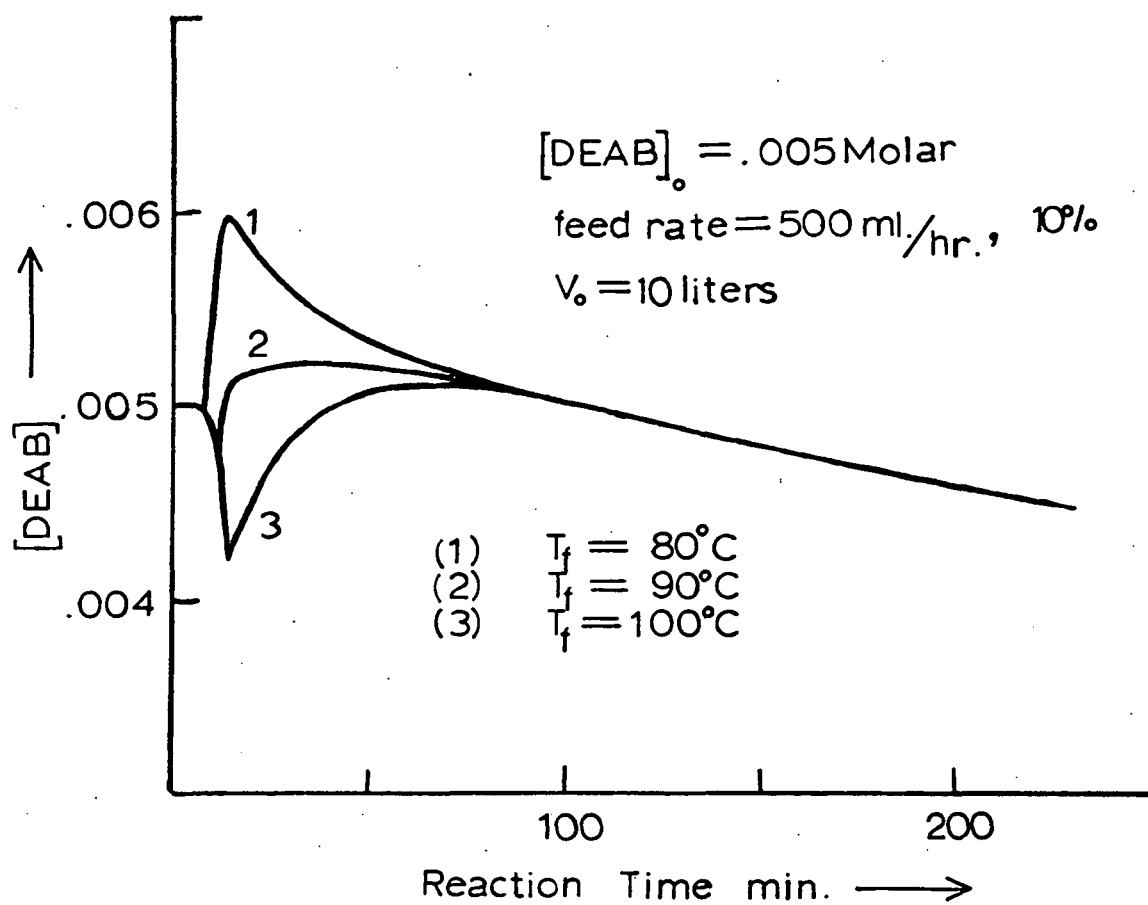


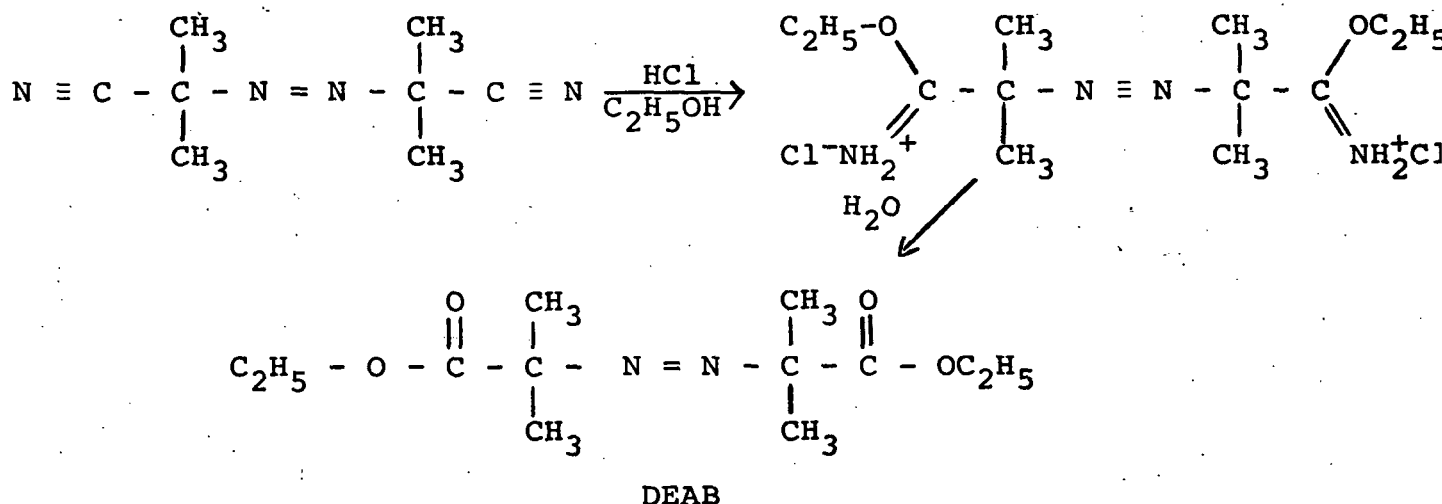
Fig.26.Effect of T_f Upon Initiator Level.

To determine the optimum feed rate and initial concentration to achieve a given initiator concentration profile, a series of simulated runs were made on the computer using feed rates of 100, 200, 300, 400, 800 and 1200 ml./hr. of 50% DEAB solution. In all runs pumping was started when the reactor temperature reached 90°C. The initial DEAB concentration for each run was determined by trial and error for the 200 ml./hr. run and merely scaled up or down to provide an appropriate starting point for the other runs. The result of these simulated runs is given in Figure 27 and the data summarized in Table XIV. In Figure 28 is shown the virtually linear relationship between $[DEAB]_m$, the initiator concentration at the mid point of a run (after 400 ml. had been fed in), and the initiator feed rate.

These results allow selection of feed schedules appropriate for the production of uniform polymer of any desired molecular weight, once the relationship between $[\text{DEAB}]_m^{-1/2}$ and $\bar{M}_n$ is determined.

c. Initiator and Monomer Preparation

A fresh supply of DEAB was prepared by treating a suspension of azobisisobutyronitrile in anhydrous ethanol with anhydrous hydrogen chloride, followed by hydrolysis of the resulting iminoether hydrochloride:



Freshly prepared DEAB has a melting point of -10 to -5°C .

M.C.&B. practical grade isoprene (93% pure by gas chromatography) was distilled through the Oldershaw column described in section C with the addition of a partial reflux head equipped with a timer. Gas chromatographic analysis of the distillate shows it to be 99.7% isoprene and 0.3% pentene-2.

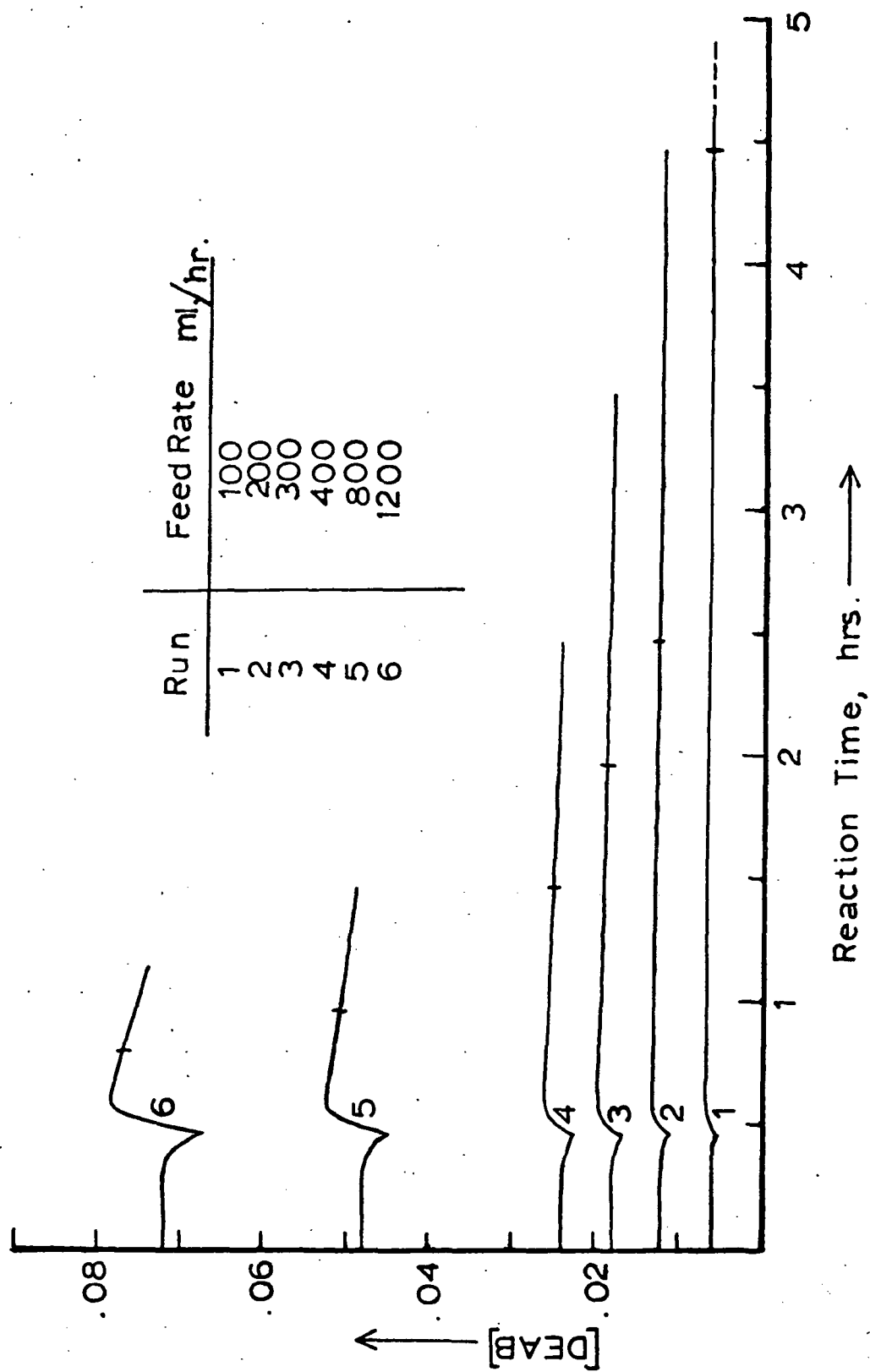


Fig.27. Relationship Between Feed Rate and DEAB Level.

TABLE XIV

RELATIONSHIP BETWEEN FEED RATE AND INITIATOR LEVEL

<u>Simulated Run No.</u>	<u>Feed Rate, Ml./Hr.</u>	$[\text{DEAB}]_0$	$[\text{DEAB}]_m$	$[\text{DEAB}]_m^{-1/2}$
1	100	.006	.0061	12.80
2	200	.012	.0124	8.98
3	300	.018	.0186	7.33
4	400	.024	.0250	6.32
5	800	.048	.0508	4.44
6	1200	.072	.0768	3.61

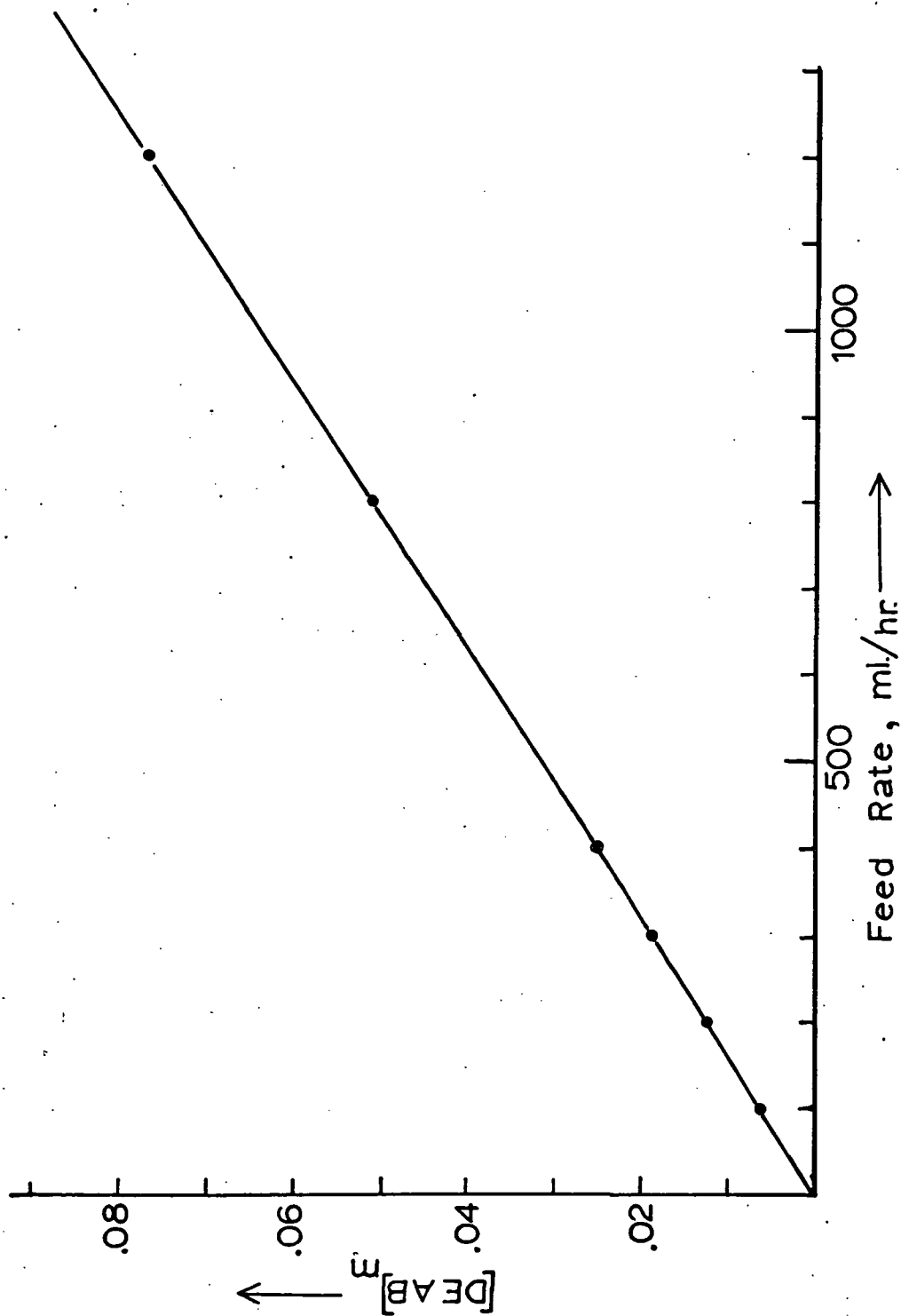


Fig.28. Initiator Concentration at Midrun, Dependence Upon Feed Rate of 50% DEAB Solution.

4. Polyisoprene Run No. 9706-ACA-105

Using the process improvements described in the preceding paragraphs, an isoprene polymerization was run in the 5-gallon reactor. Run No. 9706-ACA-105 was made with a 6820 g. (10.0 l.) charge of isoprene containing 46.5 g. DEAB. This gave a solution which was 0.018 molar in initiator. After a thorough nitrogen purge, the reactor was sealed and heated under stirring up to the polymerization temperature. When the temperature reached 90°C a 50% solution of DEAB in benzene was pumped in at a constant rate of 300 ml./hr. (This initial concentration and feed rate should give an initiator concentration profile like line 3 in Figure 27 with a DEAB concentration midway through the run of 0.0186 molar.) The polymerization temperature was controlled at 100°C ± 3° over the 2 hours 23 minutes duration of the run, during which time the pressure rose to 118 psi. When a total of 714 ml. of DEAB solution had been fed in, pumping was stopped, the internal cooling coils turned on, and the run terminated. The data are summarized in Table XV.

The unreacted isoprene was removed by vacuum evaporation on a rotary evaporator, and the residue devolatilized by passing through a falling film molecular still at 170°C/0.2 mm Hg pressure. A yield of 2495 grams (37% conversion) clear colorless liquid polymer was obtained, the functionality of which was 1.98±.02 by Vapor Pressure Osmometry ($\bar{M}_n = 2290 \pm 20$) and infrared spectroscopic analysis for ester end groups (Eq. Wt. = 1154).

A polyisoprene of 2290 $\bar{M}_n$ having end groups derived from DEAB has a number average degree of polymerization, $\bar{X}_n$, of 30.3. This fact permits us to make use of the equation in section 2C:

$$\bar{X}_n = C \frac{[M]}{[I]^{1/2}}$$

$$\text{For } [I]_m = 0.0186, \bar{X}_n = 30.3 \therefore C [M] = 30.3 \sqrt{.0186} = 4.13$$

Having evaluated this product, we can select a concentration of DEAB required to give any desired molecular weight product.

$$\text{Since } \bar{X}_n = \frac{\bar{M}_n - 230}{68}$$

$$\text{We have } [I] = \left[\frac{4.13}{(\bar{M}_n - 230)/68} \right]^2$$

Thus to prepare a 3000 molecular weight ester telechelic polyisoprene, the initiator concentration required is:

$$[I] = \left[\frac{4.13}{(3000-230)/68} \right]^2 = 0.0103$$

And, according to Figure 27, a feed rate of about 170 ml./hr. would be required using a 50% DEAB solution.

TABLE XV

5-GALLON BATCH ISOPRENE POLYMERIZATION

<u>RUN NO. 9706-</u>	105
<u>Charged Initially</u>	
Isoprene, gms.	6820
DEAB, gms.	46.5
DEAB _o , molar	0.0180
<u>Fed During Run</u>	
Ml. 50% DEAB/Benzene	714
Feed Rate, ml./hr.	300
DEAB _m , molar ^a	0.0186
<u>Reaction Conditions</u>	
Temperature ^b	97-104°C
Pressure, psi	70-116
Total Time	2 hrs. 23 min.
<u>Productivity</u>	
Yield, gms	2,495
Conversion, %	37
Conversion Rate, %/hr.	15
<u>Product Description</u>	
Appearance	Clear, colorless liquid
M _n (V.P.O. in toluene, 37°C)	2290±20
Ester Equivalent Weight (infrared)	1154
Ester Functionality	1.98±.02

a. From Figure 27.

b. After reaching control temperature.

- APPENDIX 4

SIMULATION OF THE FIVE GALLON REACTOR BY ANALOG PROGRAMMING -
INITIATOR FEED SYSTEM AND DECOMPOSITION KINETICS

As described earlier, we have used the IBM application program "1130 Continuous System Modeling Program", 1130-CX-13X. This program provides the investigator with a convenient and versatile tool for simulating the behavior of complex systems. It is a "digital analog simulator" using a block-oriented input language in which the functional blocks represent the elements and organization of an analog computer. Once the analog model of a system has been specified, online interaction is possible allowing the user to modify the system, change parameters, etc. with a minimum of difficulty.

The system we have chosen to simulate is the 5-gallon, well stirred reactor having an initial volume, V_0 , an initial concentration of initiator, I_0 , and an initial temperature, T_0 . A realistic temperature profile (experimentally determined) is assumed, together with an upper temperature limit at which the reactor is temperature controlled, T_f , in this case $T_f = 100^\circ\text{C}$. The system contains a pump which feeds a solution of initiator at a specified concentration into the reactor at two different rates, P_1 and P_2 . Control of the pump from P_1 (in our case $P_1 = 0$) to P_2 is accomplished by a relay element which switches when a specified Temperature, T_p is reached by the reactor.

The kinetics of decomposition of the initiator are assumed to be simple first order in form:

$$\frac{-dI}{dt} = K \times I,$$

with the temperature behavior of the rate constant given by Arrhenius equation:

$$K = Ae^{-\Delta E/RT}$$

The experimentally determined values for the energy of activation and the frequency factor were used:

$$\Delta E = 30,908 \text{ k cal/mole}$$

$$A = 6.5 \times 10^{16} \text{ min.}^{-1}$$

The simulation must therefore satisfy the following differential equation: --

$$\frac{dI}{dt} = \frac{P/C}{V_0 + Pt} - KI,$$

where the feed rate, P , has two allowed values and K is continuously variable as T increases from T_0 to 100°C .

The block diagram shown in Fig. 29 was next assembled (See symbolic key, Fig. 30). Blocks 1, 23, 24, 25, 26 and 151 together comprise the temperature program. Block 1 contains in tabular form the experimental heating curve for the 5-gallon reactor with a 10-l charge in it. Block 26 is a relay element which switches over to a constant final temperature T_m after the initial heating-up phase. The output of this block is the reactor temperature.

Blocks 6, 18, 19, 34, 35, 36 and 37 together comprise the initiator pumping program. At a preset temperature (in block 37) the relay element 35 switches from the initial pumping rate P_1 (usually zero) to the rate used during the polymerization. Blocks 7, 8, 20 and 22 keep track of the system volume based upon the initial volume V_0 and the pumping rate $P' = P/C$. Blocks 9, 10, 21, 38 and 39 provide the derivative of initiator concentration as supplied by the pump by giving the rate of addition of initiator in moles/min. (output of block 10) divided by the system volume.

Blocks 2, 3, 4, 5, 15, 16 and 27 represent the Arrhenius equation. From known constants and the temperature output of block 26, this subprogram calculates the rate constant as the temperature of the reactor changes from T_0 up to T_m .

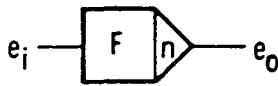
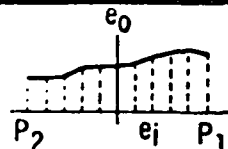
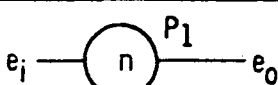
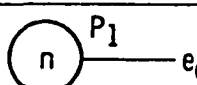
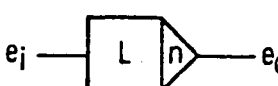
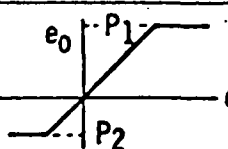
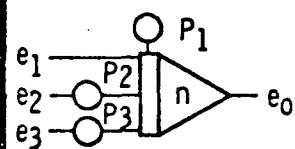
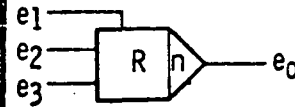
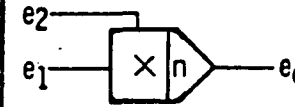
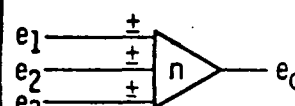
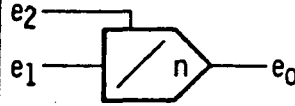
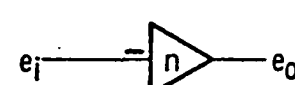
Blocks 11, 12, 13 and 14 actually perform the integration of the differential equation. Block 11 receives both derivatives $d_1 = -P/CV$ and $d_2 = KI$ and the negative of the initial initiator concentration $-I_0$, integrates them and provides $-I$ as output for the inverter and limiter elements 12 and 13.

Having specified the model in symbolic form, it is next translated into card input for CSMP (Continuous Systems Modeling Program). On a one-line-per-card basis, this card input is identical to the output (less column headings) shown in Figure 30 and the top half of Figure 31. When CSMP is loaded and the card deck specifying the model is fed in, a dialogue between computer and operator takes place during which other specifications such as integration interval, total time for run, output variables etc., are entered. When this has been done, the results are provided by the computer in both tabular (Fig. 32) and graphical form (Fig. 33) if desired.

A very flexible interaction is then possible between operator and computer in which the system parameters, or even the configuration, can be modified at will and subsequent "runs" made upon the modified system.



Fig.29. Flow Chart, Analog Simulation of Initiator Feed System and Initiator Decomposition Kinetics.

ELEMENT TYPE	LANGUAGE SYMBOL	DIAGRAMMATIC SYMBOL	DESCRIPTION
FUNCTION GENERATOR	F		
GAIN	G		$e_o = P_1 e_i$
CONSTANT	K		$e_o = P_1$
LIMITER	L		
INTEGRATOR	I		$e_o = P_1 + \int (e_1 + e_2 P_2 + e_3 P_3) dt$
RELAY	R		$e_o = \begin{matrix} e_2 & \text{for } e_1 \geq 0 \\ e_3 & \text{for } e_1 < 0 \end{matrix}$
MULTIPLIER	X		$e_o = e_1 e_2$
SUMMER	+		$e_o = \pm e_1 \pm e_2 \pm e_3$ ONLY ELEMENT WHERE NEGATIVE SIGN IS PERMISSIBLE IN CONFIGURATION SPECIFICATION
DIVIDER	/		$e_o = e_1 / e_2$
SIGN INVERTER	-		$e_o = -e_i$
SPECIAL	1-5		SUBROUTINES SUPPLIED BY USER

n REPRESENTS THE BLOCK NUMBER

FIG. 30. KEY TO SYMBOLS USED IN FIG. 29.

CONTINUOUS SYSTEM MODELING PROGRAM
A DIGITAL ANALOG SIMULATOR PROGRAM FOR THE IBM 1130

CONFIGURATION SPECIFICATION

OUTPUT NAME	BLOCK	TYPE	INPUT 1	INPUT 2	INPUT 3
	1	F	151	0	0
	25	+	151	-23	0
TMAX, DEG. K	24	K	0	0	0
TIME TO TMAX	23	K	0	0	0
TEMP., DEG. K	26	R	25	24	1
GAS CONST.	15	K	0	0	0
DELTA E	16	K	0	0	0
	2	/	16	15	0
	27	-	2	0	0
	3	/	27	26	0
	4	1	3	0	0
DECOMP. RATE	5	G	4	0	0
TEMP AT PUMP CHG	37	K	0	0	0
SET POINT	36	+	26	-37	0
PUMP CONTROL	35	R	36	19	34
FEED RATE ML/HR	19	K	0	0	0
INIT PUMP RATE	34	K	0	0	0
C1	18	K	0	0	0
	6	/	35	18	0
	7	1	6	0	0
INITIAL VOLUME L	20	K	0	0	0
VOLUME	8	+	7	20	0
	22	-	8	0	0
MOL. WT. INIT.	21	K	0	0	0
FEED SOLN. CONC.	38	K	0	0	0
	39	X	6	38	0
	10	/	39	21	0
	9	/	10	22	0
	11	1	9	14	0
CONCENTRATION	12	-	11	0	0
LIM. CONC.	13	L	12	0	0
	14	X	13	5	0
HALF LIFE	32	/	33	5	0
	33	K	0	0	0

FIG. 31. CSMP OUTPUT, PAGE 1.

INITIAL CONDITIONS AND PARAMETERS

IC/PAR NAME	BLOCK	IC/PAR1	PAR2	PAR3
FGTL	1	50.0000	0.0000	0.0000
TIME TO TMAX	23	50.0000	0.0000	0.0000
TMAX	24	373.0000	0.0000	0.0000
GAS CONST.	15	1.9870	0.0000	0.0000
DELTA E	16	30908.0039	0.0000	0.0000
A	5	0.6501E 17	0.0000E 00	0.0000E 00
C1	18	60000.0079	0.0000	0.0000
NORM FEED RATE	19	100.0000	0.0000	0.0000
INIT. FEED RATE	34	0.0000	0.0000	0.0000
FEED VOL.	7	0.0000	0.0000	0.0000
TEMP START FEED	37	363.0000	0.0000	0.0000
INITIAL VOLUME, L	20	10.0000	0.0000	0.0000
FEED SOLN CONC	38	500.0000	0.0000	0.0000
MOL WT INITIATOR	21	258.5200	0.0000	0.0000
INIT DEAB CONC	11	-0.0060	1.0000	0.0000
LIMITS	13	4.0000	0.0000	0.0000
	33	0.6930	0.0000	0.0000

FUNCTION GENERATOR SPECIFICATIONS

1	283.0000	291.0000	307.0000	330.0000
	348.0000	358.0000	366.0000	373.0000
	373.0000	373.0000	373.0000	

(1.0) INTEGRATION INTERVAL

(300.) TOTAL TIME

(13) BLOCK FOR Y-AXIS (0.) MINIMUM VALUE (.02) MAXIMUM VALUE

(151) BLOCK FOR X-AXIS (0.) MINIMUM VALUE (300.) MAXIMUM VALUE

(0) PLOT POINTER

(5.) PRINT INTERVAL

FIG. 31. CSMP OUTPUT, PAGE 2. USER RESPONSE IS UNDERLINED.

TIME	-94-				
	OUTPUT() <u>26</u>	OUTPUT() <u>32</u>	OUTPUT() <u>14</u>	OUTPUT() <u>7</u>	OUTPUT() <u>13</u>
0.000	0.2830E 03	0.7920E 07	0.5249E-09	0.0000E 00	0.6000E-02
5.000	0.2910E 03	0.174ZE 07	0.2378E-08	0.0000E 00	0.5999E-02
10.000	0.3070E 03	0.1078E 06	0.3857E-07	0.0000E 00	0.5999E-02
15.000	0.3300E 03	0.3154E 04	0.1317E-05	0.0000E 00	0.5998E-02
20.000	0.3480E 03	0.2754E 03	0.1501E-04	0.0000E 00	0.5969E-02
25.000	0.3580E 03	0.7904E 02	0.5103E-04	0.0000E 00	0.5821E-02
30.000	366.00006	30.57698	0.00013	0.00333	0.00604
35.000	373.00006	13.77224	0.00032	0.01166	0.00654
40.000	373.00006	13.77224	0.00032	0.01999	0.00651
45.000	373.00006	13.77224	0.00032	0.02833	0.00648
50.000	373.00006	13.77224	0.00032	0.03666	0.00646
55.000	373.00006	13.77224	0.00032	0.04499	0.00644
60.000	373.00006	13.77224	0.00032	0.05333	0.00643
65.000	373.00006	13.77224	0.00032	0.06166	0.00641
70.000	373.00006	13.77224	0.00032	0.06999	0.00640
75.000	373.00006	13.77224	0.00032	0.07833	0.00639
80.000	373.00006	13.77224	0.00032	0.08666	0.00638
85.000	373.00006	13.77224	0.00032	0.09499	0.00638
90.000	373.00006	13.77224	0.00032	0.10333	0.00637
95.000	373.00006	13.77224	0.00032	0.11166	0.00636
100.000	373.00006	13.77224	0.00032	0.11999	0.00636
105.000	373.00006	13.77224	0.00031	0.12833	0.00635
110.000	373.00006	13.77224	0.00031	0.13666	0.00634
115.000	373.00006	13.77224	0.00031	0.14499	0.00634
120.000	373.00006	13.77224	0.00031	0.15333	0.00633
125.000	373.00006	13.77224	0.00031	0.16166	0.00633
130.000	373.00006	13.77224	0.00031	0.16999	0.00632
135.000	373.00006	13.77224	0.00031	0.17833	0.00632
140.000	373.00006	13.77224	0.00031	0.18666	0.00631
145.000	373.00006	13.77224	0.00031	0.19499	0.00630
150.000	373.00006	13.77224	0.00031	0.20333	0.00630
155.000	373.00006	13.77224	0.00031	0.21166	0.00629
160.000	373.00006	13.77224	0.00031	0.21999	0.00629
165.000	373.00006	13.77224	0.00031	0.22833	0.00628
170.000	373.00006	13.77224	0.00031	0.23666	0.00628
175.000	373.00006	13.77224	0.00031	0.24499	0.00627
180.000	373.00006	13.77224	0.00031	0.25333	0.00627
185.000	373.00006	13.77224	0.00031	0.26166	0.00626
190.000	373.00006	13.77224	0.00031	0.26999	0.00626
195.000	373.00006	13.77224	0.00031	0.27833	0.00625
200.000	373.00006	13.77224	0.00031	0.28666	0.00625
205.000	373.00006	13.77224	0.00031	0.29499	0.00624
210.000	373.00006	13.77224	0.00031	0.30333	0.00624
215.000	373.00006	13.77224	0.00031	0.31166	0.00623
220.000	373.00006	13.77224	0.00031	0.31999	0.00623
225.000	373.00006	13.77224	0.00031	0.32833	0.00622
230.000	373.00006	13.77224	0.00031	0.33666	0.00622
235.000	373.00006	13.77224	0.00031	0.34499	0.00621
240.000	373.00006	13.77224	0.00031	0.35333	0.00621
245.000	373.00006	13.77224	0.00031	0.36166	0.00620
250.000	373.00006	13.77224	0.00031	0.36999	0.00620
255.000	373.00006	13.77224	0.00031	0.37833	0.00619
260.000	373.00006	13.77224	0.00031	0.38666	0.00619
265.000	373.00006	13.77224	0.00031	0.39499	0.00618
270.000	373.00006	13.77224	0.00031	0.40333	0.00618
275.000	373.00006	13.77224	0.00031	0.41166	0.00617
280.000	373.00006	13.77224	0.00031	0.41999	0.00617
285.000	373.00006	13.77224	0.00031	0.42833	0.00616
290.000	373.00006	13.77224	0.00031	0.43666	0.00616
295.000	373.00006	13.77224	0.00030	0.44499	0.00615
300.000	373.00006	13.77224	0.00030	0.45333	0.00615

FIG. 32. CSMP OUTPUT, PAGE 3 - TABULAR RESULTS.

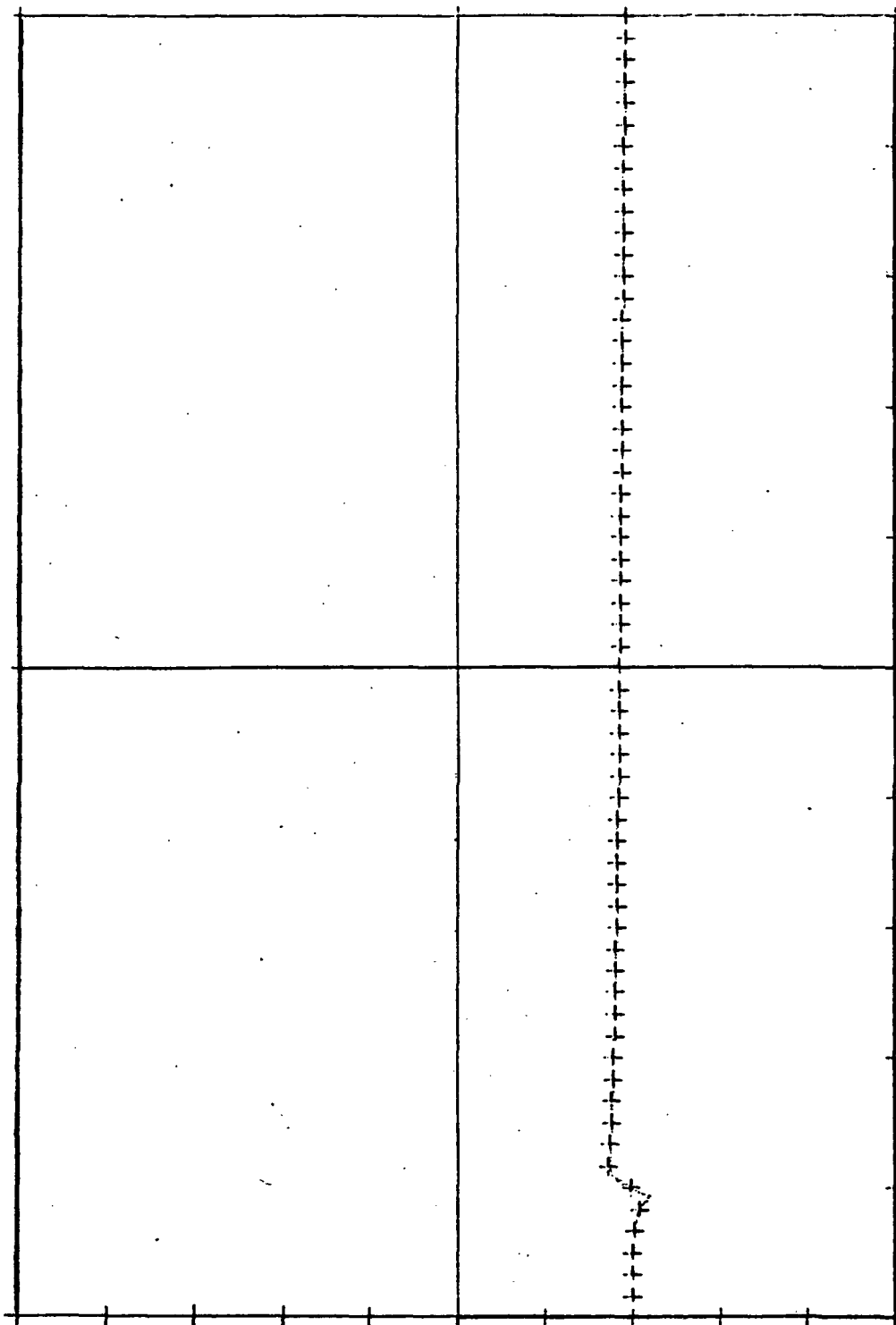


FIG. 33. CSMP OUTPUT, PAGE 4 - GRAPHICAL RESULTS.

APPENDIX 5

TWO DIMENSIONAL THIN LAYER CHROMATOGRAPHY APPLIED
TO THE ANALYSIS OF HYDROXYL TELECHELIC PREPOLYMERS

We have had considerable success in the analysis of low molecular weight hydroxyl and carboxyl telechelic polymers for functionality distribution using the technique of thin layer chromatography (TLC).¹⁴ This is especially useful in narrow molecular weight distribution prepolymers such as those produced by anionic living polymerization. In such prepolymers, development of TLC plate in a solvent such as methylene chloride or 1% ethanol in neptane results in a chromatogram in which the di-, mono- and non-functional fractions are completely resolved. When this technique is applied to higher molecular weight prepolymers, or especially to prepolymers having a broader molecular weight distribution, one frequently finds that the fractions are elongated into extended spindle shaped streaks on the plates. This results in the overlap of, for example, the higher molecular weight (and therefore less polar) components of the difunctional fraction onto the lower molecular weight (and therefore more polar) components of the monofunctional fraction. The limit of this behavior is the loss of all resolution giving rise to chromatograms consisting of a single elongated streak, even when the sample is heterogeneous with regard to functionality distribution.

We have found that the use of acetone, which is a poor solvent for the hydrocarbon prepolymers, as a second eluting agent at right angles to the first development, transforms these useless overlapping chromatograms into a two dimensional chromatogram consisting of a family of S-shaped curves, well resolved from each other. Four two dimensional thin layer chromatograms prepared using this technique are shown in figure 34.

In these chromatograms, spots were applied at three corners of the plate and the first development performed in the vertical direction using an eluting solvent found to give good separation on the basis of functionality. A, B and D were developed using 2% Ethanol in benzene, C with 1% Ethanol in heptane. This results in a one dimensional chromatogram from two of the three spots. The plate is then dried in a vacuum oven and placed in a second chamber for development in acetone at right angles to the first development. This results in a one dimensional chromatogram from the third spot, and a second

14) See page 195 in our triennial report.

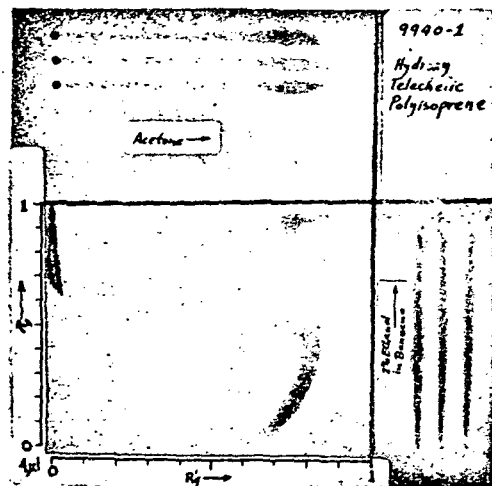
development resulting in a two dimensional chromatogram, for the second spot. The first spot is unaffected by the second development. We thus have on a single plate two ordinary thin layer chromatograms in two different solvents and one two-dimensional chromatogram in both solvents.

The beneficial effect of the second development in acetone we believe to result from the fact that only the low molecular weight fraction of the hydrocarbon prepolymers is appreciably soluble in acetone. This fraction is thus free to migrate on the plate and moves to high R_f values since the silica on the plate is thoroughly deactivated by the polar solvent acetone. The high molecular weight fraction however is not free to migrate since it does not dissolve in the eluting solvent and thus remains near $R_f = 0$.

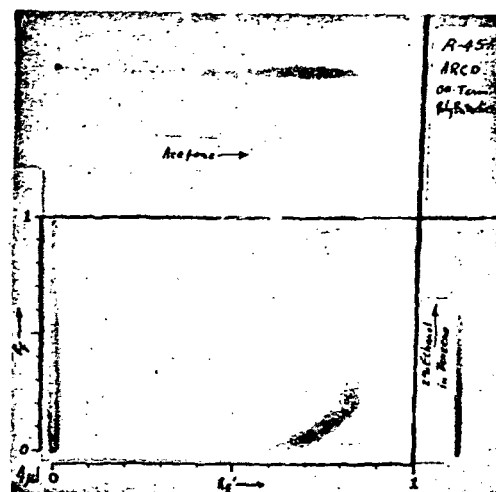
This effect is easily seen in chromatogram A of a strictly difunctional hydroxy telechelic polyisoprene. On the right hand margin of the plate are the spots which received only one development in 2% ethanol in benzene. No resolution is possible since the chromatogram covers the whole range from $R_f = 0$ to $R_f = 1$. On the top of the plate are the spots which received a single development in acetone. The low molecular weight fraction has been eluted up to $R_f \sim .6$ to $.8$ leaving the high molecular weight fraction trailing behind and as a spot at the origin. The spot applied at the lower left hand corner was a streak at $R_f = 0$, $R_f = 0$ to 1 after the first development. The second development effectively pushed the $R_f = 0$ to $.6$ section to the right, to $R_f = .6$ to $.8$, giving the S-shaped streak shown.

Chromatograms C and D were included to show how a truly heterogenous prepolymer would behave under these conditions. (Note reversal of development direction in C). This prepolymer was prepared by adding one half the required amount of "Vitride"* reducing agent to a telechelic difunctional ester terminated polyisoprene. This partial reduction resulted in a statistical mixture of diester (non-functional with regard to hydroxyl), ester-alcohol (monofunctional) and diol (difunctional). Chromatogram C was prepared from this product. Note the complete separation of all three components. Chromatogram D was prepared 5 months later after the 10% benzene solution had been stored in contact with the air. Some oxidative degradation with the formation of crosslinks is suggested by the presence of a new component at $R_f = 0$ to $.05$ and $R_f = .4$ to $.9$. We suggest that this component is trifunctional or higher in functionality and results from oxidative coupling of difunctional molecules (or di- with mono-) during the 5 month storage period in solution. Thus chromatograms C and D demonstrate the ability of the 2-D TLC method to resolve complex functionality distributions. A hand retouched xerox copy of plate D is given in Figure 35 to serve as a key to assist in the reader in interpreting the photographs in Figure 34. Similarly Figure 36 is a full size copy of plate A of Figure 34.

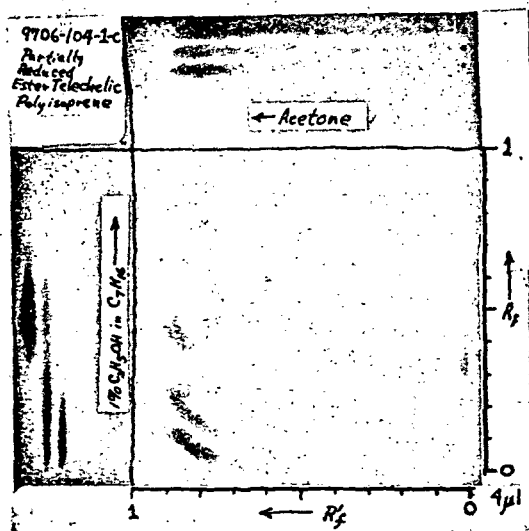
* "Vitride" is sodium bis [methoxyethoxy] aluminum hydride manuf. by the reAlco Corp. It is chemically equivalent to LiAlH_4 but is safer and more convenient to use.



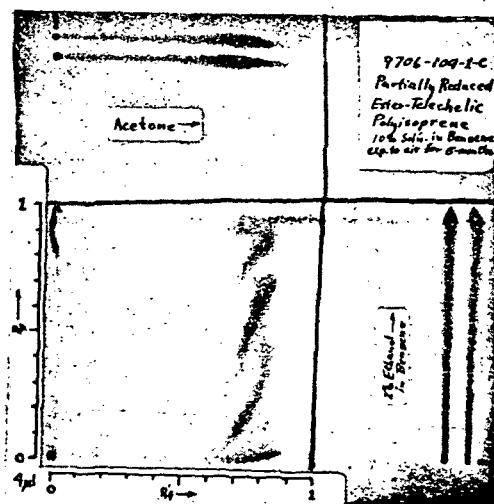
A



B



C



D

Fig. 34. Two Dimensional TLC Analysis of Hydroxyl Terminated Prepolymers

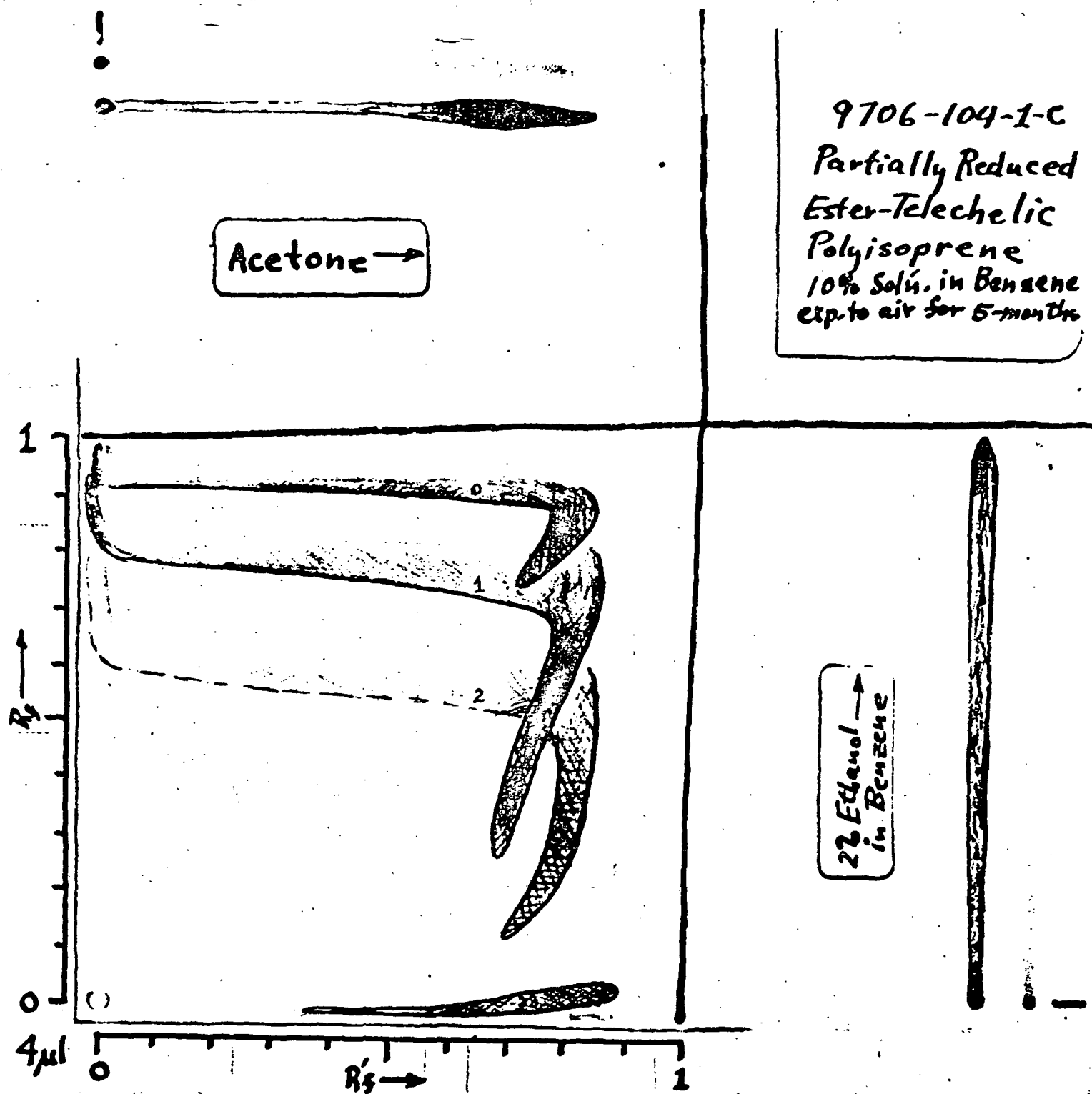


FIG. 35. TWO DIMENSIONAL TLC ANALYSIS OF A PARTIALLY
REDUCED ESTER-TELECHELIC POLYISOPRENE

9940-1

Hydroxy
Telechelic
Polyisoprene

Acetone →

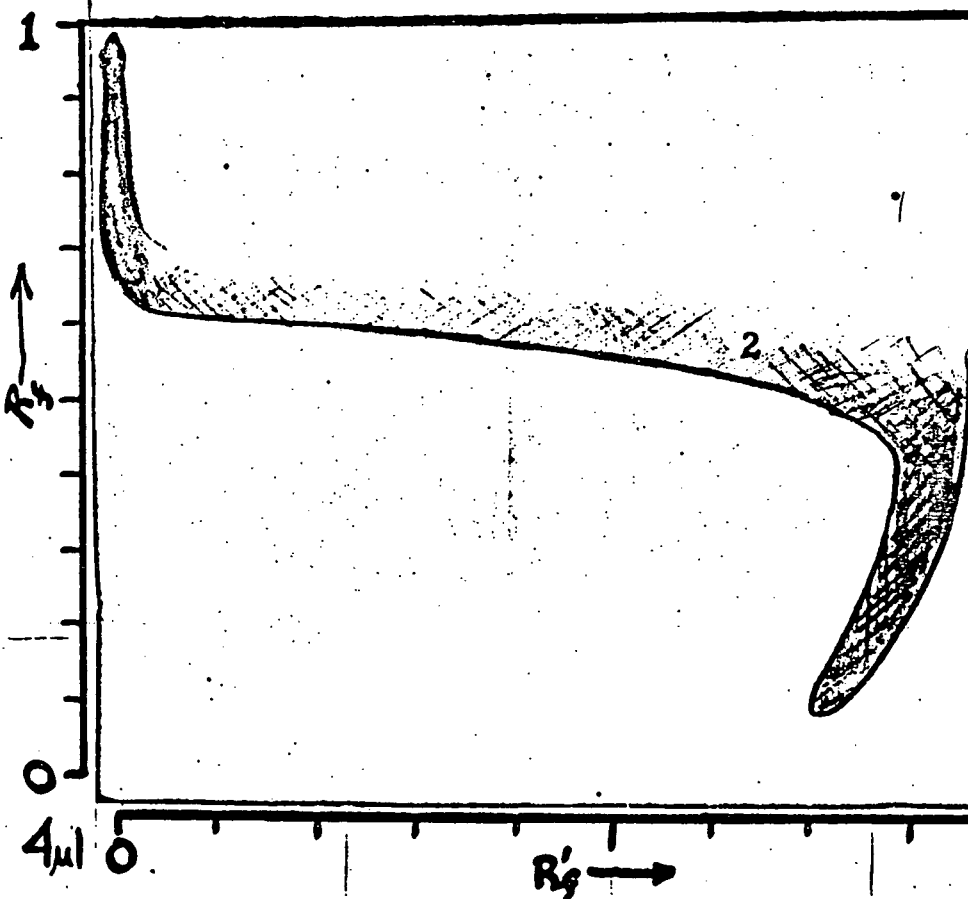


FIG. 36. TWO DIMENSIONAL TLC ANALYSIS OF A
HYDROXY TELECHELIC POLYISOPRENE

Plate B is included to illustrate the utility of the 2-D TLC method upon other than polyisoprene prepolymers.

The product R-45-HT is a hydroxyl terminated polybutadiene supplied by the ARCO Corporation. This product has a number average molecular weight of 2750 and a hydroxyl equivalent weight of 1238 ± 14 by acetylation. It, therefore, has an average functionality of 2.22 and must contain components having a functionality greater than two. This product is similar to R-45-M which has been well characterized by A. H. Muenker¹⁵ and found to contain a trifunctional component. Note the appearance of a streak at $R_f = 0$ to .05 and $R_f = .4$ to .9. This is the same location as the >3 functionality component noted in chromatogram D.

In prepolymers containing a significant fraction of 3 or greater functionality molecules, a more strongly eluting solvent, say 5% ethanol in benzene, would be preferred for the first development of 2-D TLC analysis.

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15. A. H. Muenker, "Determination of Prepolymer Functionality and its Relationship to Binder Properties", interim technical report February 3, 1969 to August 31, 1969, AFRPL-TR-69-214.

VI. PLANS FOR FUTURE WORK

We plan to prepare a twenty pound sample of a hydroxyl-telechelic polyisoprene using the five gallon stirred autoclave reactor. This will be accomplished by making 4-5 sequential runs under identical conditions and compositing to give the product. This will be reduced with a hydride reducing agent to give sufficient prepolymer for larger scale evaluation at J. P. L.

We also plan to refine the chain structure of our saturated hydrocarbon prepolymers with the goal being the production of a saturated product having the desirable viscosity and low temperature properties of the unsaturated hydrocarbon prepolymers.

VII. NEW TECHNOLOGY

Item 1 -

U. S. Patent Application #148992
James E. Potts
Arnold C. Ashcraft, Jr.
Edgar W. Wise

Title: Terminally Difunctional Liquid Hydrocarbon
Polymers By Free Radical Polymerization

Date Revealed to NASA: November 26, 1968

Reports: See Section V-3 of this Report.

Item 2 -

A two dimensional thin layer chromatographic analysis has been perfected which allows the determination of functionality distribution in hydroxyl telechelic prepolymers where the molecular weight distribution of the prepolymer causes one dimensional chromatography to be ineffective.

ACA/JEP/EWW:jvd, pk, km